

ReCell Advanced Battery Recycling Center

First/Second Quarter Progress Report 2019

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Table of Contents

Overview	2
Milestone FY19Q1/Q2	4
Direct Cathode Recycling	6
Chemical Relithiation (Argonne)	7
Electrochemical Relithiation (NREL)	10
Ionothermal Relithiation (ORNL)	13
Hydrothermal Relithiation (UCSD)	17
Binder Removal (Argonne)	22
Cathode/Cathode Separation (Argonne)	24
Cathode/Cathode Separation via Froth Flotation (MTU)	26
Role of Impurities in Recycled Cathodes (WPI)	29
Cathode Composition Change (Argonne)	33
Recovery of Other Materials	35
Electrolyte Component Removal and Recovery (Argonne)	36
Hydrothermal Recovery Process for Black Mass (ORNL)	39
Anode/Cathode Separation and Purification (Argonne)	43
Design for Recycle	45
Cell Design (Argonne/ORNL)	46
Modeling and Analysis	49
Diagnostics of Aged Materials (NREL)	50
Microcalorimetry of Recycled Materials (NREL)	52
Cost and Environmental Impact Modeling: EverBatt (Argonne)	54
Supply Chain Analysis for Battery Recycling (NREL)	56
Crosscutting Efforts	
CAMP Support (Argonne)	58
Post Test Support (Argonne)	61

Overview

The use of lithium-ion batteries has surged in recent years, starting with electronics and expanding into many applications, including the growing electric and hybrid vehicle industry. But the technologies to optimize recycling of these batteries has not kept pace.

The launch of the U.S. Department of Energy's (DOE) first lithium-ion battery recycling center, called the ReCell Center, will help the United States grow a globally competitive recycling industry and reduce our reliance on foreign sources of battery materials.

The DOE sees an opportunity to de-risk the recycling of lithium-ion batteries and future battery chemistries to help accelerate the growth of a profitable recycling market for spent EV and electronics batteries. This can be done by developing novel recycling techniques that will make lithium-ion recycling cost-effective by using less energy-intensive processing methods and capturing more metals and other high-value materials in forms that make reuse easier.

Accelerating and advancing industry adoption of EV battery recycling will help meet the Vehicle Technology Office goals of pushing down the cost of EV battery packs for consumers and increasing the use of domestic recycled sources of battery materials.

These recycled materials can be recycled for use in new batteries, helping to drive down the overall production cost of electric vehicle batteries to the national goal of \$80/kWh.

A collaboration of researchers from industry, academia and national laboratories will test new recycling techniques at their home institutions and at Argonne National Laboratory in order to develop new battery designs that will enable greater material recovery at end of life. The most promising new recycling processes and battery designs will be demonstrated at pilot scale at the ReCell Center based at Argonne. Validated processes and designs will be licensed to industry for further commercialization.

The center collaborators also will use existing modeling and analysis tools to help industry determine how to optimize value. Argonne's EverBatt model evaluates the techno-economic and environmental impacts of each stage of a battery's life, including recycling. NREL's supply chain analysis tool provides a birds-eye view of the interconnections between raw material availability, primary manufacture, recycling, and demand.

The ReCell Center had its kickoff meeting November 1-2, 2018, at Argonne National Laboratory. The three laboratory partners (Argonne National Laboratory, National Renewable Laboratory, and Oak Ridge National Laboratory) were all present, as well as the three collaborating universities (University of California San Diego, Worcester Polytechnic Institute, and Michigan Technological University). The center organization is shown in Figure 1.

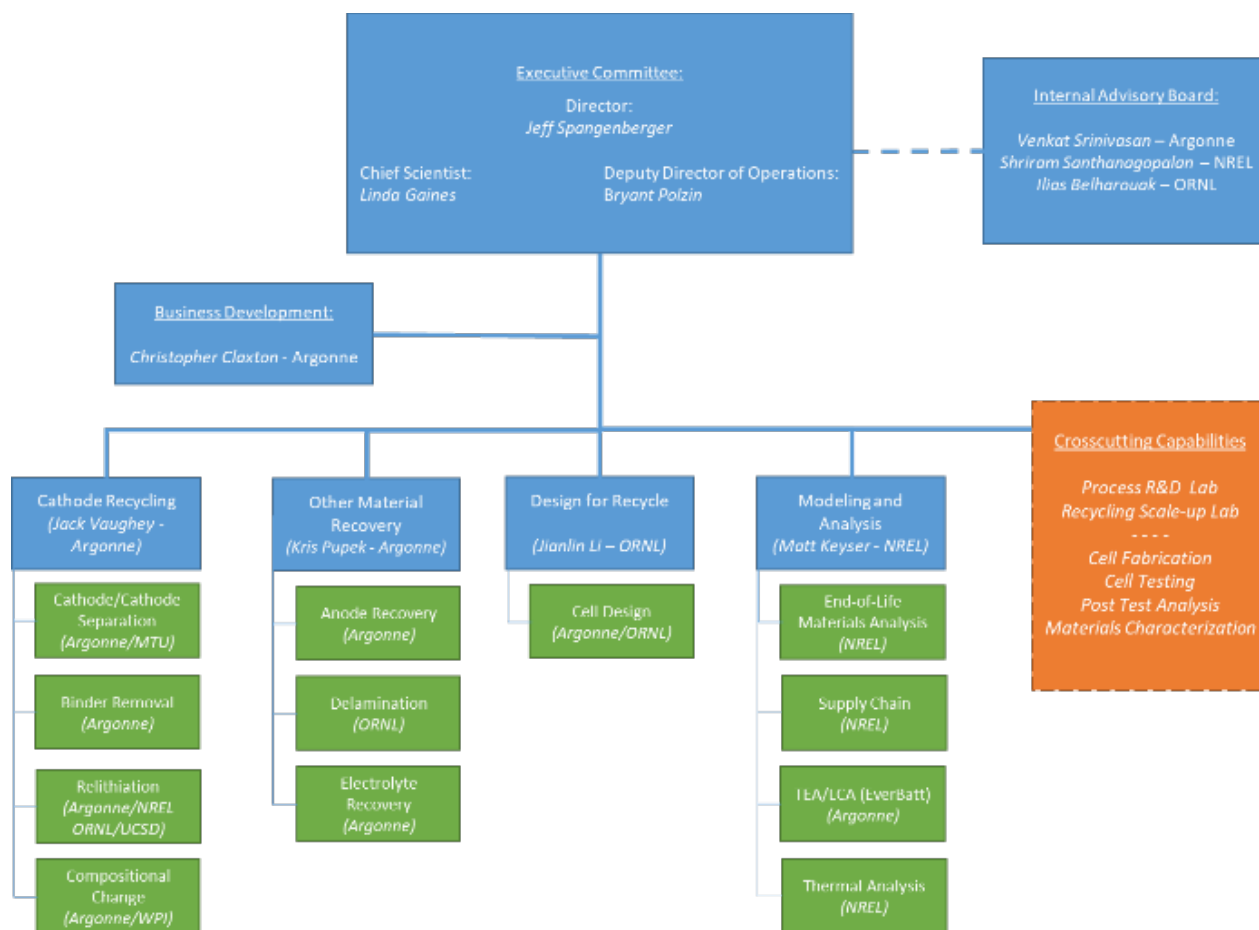


Figure 1. ReCell organization chart as of the end of FY19Q2

The four focus areas include Direct Cathode Recycling, Recovery of Other Materials, Design for Recycle, and Modeling and Analysis. A total of 17 projects across the four focus areas identified as the initial work to be performed within the center.

In addition to the focus areas, each organization has crosscutting capabilities that will be utilized throughout this program.

Energy Secretary Rick Perry announced the ReCell Center on January 17, 2019 (at the Bipartisan Policy Center's American Energy Innovation Council) as a national security initiative that will bolster economic growth, strengthen our energy security and improve the environment. Daniel Simmons, Assistant Secretary for Energy Efficiency and Renewable Energy, and Alex Fitzsimmons, Chief of Staff for the Office of Energy Efficiency and Renewable Energy, and many others joined the ribbon-cutting celebration on February 15th, 2019 at Argonne that will house equipment for scale-up demonstrations. Bench- and pilot-scale laboratories are under construction at Argonne and scheduled to be completed at the end of FY19.

Milestone FY19Q1/Q2

The center's FY19Q1 milestone was to establish a mission. The team decided upon the following mission:

“Decrease the cost of recycling lithium-ion batteries to ensure future supply of critical materials and decrease energy usage compared to raw material production”

The mission recognizes that a profitable infrastructure will enable responsible battery recycling practices. A steady supply of end-of-life batteries to recyclers, driven by economics, will enable the recovery and reuse of the critical materials providing an increased level of national security. In addition, energy use and emissions can be reduced compared to production from mining.

The FY19Q2 milestone is an initial progress report on roll-to-roll relithiation. Early work on this project utilizes a chemically delithiated NMC cathode powder. This was done so a pseudo-capacity reduced cathode material could more easily be obtained, enabling scoping work to be performed. The chemically delithiated cathode was determined to be comparable to actual cycled cathode materials.

The early stages of work on the roll-to-roll relithiation used coin cells to provide proof of concept testing. Chemically delithiated electrodes were cast and cycled against lithium metal anodes to add lithium back into the cathode. The cells, with the relithiated cathode, were then taken apart, and the cathode matched with a graphite anode to compare the performance to a pristine system. Capacity was found to be reduced due to consumption of lithium by the formation of the SEI on the unformed anode. The initial degree of relithiation is being explored along with the use of pre-formed anode electrodes. More information is located in the project report section of this document.

Project Reports

There are a total of 17 individual projects and two crosscutting reports that follow. The reports are grouped by their focus areas, but are in no special order.

Direct Recycle

In 2018, production of lithium-ion batteries (LIB) in the world consumed > 50,000 tons of various transition metals and lithium salts to meet the world's energy storage needs. For the manufacture of LIBs, the consumption of these critical materials is at the scale where they represent a significant market for suppliers, mineral companies, and materials processors. Most notably, at present rates of production, over 50% of the world's output of cobalt is used to make LIBs, with projections that demand will increase significantly as various countries attempt to reduce fossil fuel consumption. An alternative to increased mine output and exploration is to utilize recycling of out of service LIBs as a source of various critical metals or as a feedstock for new low-cobalt compositions. Within this program we are seeking to understand how to address the various types of cathode materials that are used in the marketplace, the state of their performance at end-of-life, and to develop processes to, with minimal input, recover, rejuvenate, and reuse these cathode electrode materials. In this section we are seeking to address the issue that at end of life, due to side reactions, salt precipitation, and corrosion, the amount of useable lithium within the cathode structure is typically about 15-20% below the initial formulation, e.g. $\text{Li}_{0.8}(\text{Ni}_{0.33}\text{Mn}_{0.33}\text{Co}_{0.33})\text{O}_2$. Within direct cathode recycling, there are four efforts focused on cathode separation and isolation processes (froth flotation, magnetic separation, electrode binder removal, impurity incorporation into the cathode), four pathways that seek to address relithiation of the recovered cathode (chemical relithiation, electrochemical relithiation, ionothermal relithiation, and hydrothermal relithiation) and will be evaluated in terms of relithiation extent, relithiation rate, and eventually by cost of the relithiation process (with Q. Dai, EverBatt Model). In addition, an effort that addresses the role of altering the metal ratio will be undertaken, focused on using the relithiated Co-rich cathodes as feedstock for low-Cobalt, Ni-rich cathodes.

Chemical Relithiation

Tony Montoya, Jack Vaughey (Argonne)

Background

One of the main causes of performance degradation for cathode lithium-ion battery materials is the gradual cycle to cycle loss of active lithium. Due to SEI formation, corrosion, and electronic isolation of particles, the active lithium initially supplied by the NMC cathode can be irreversibly trapped in a variety of forms that affects the battery performance. On long term usage, the amount of lithium trapped and rendered inactive increases at a slow rate (after losses involved in the initial break-in cycling), gradually decreasing the cells capacity until performance is noticeably affected or the commonly used 80% of initial capacity value is reached. At this point a commonly observed stoichiometry of $\text{Li}_{0.9}(\text{NiMnCo})\text{O}_2$ has been determined analytically. The structure of this end of life (EoL) product is a lithium deficient version of the starting materials, although some further structural changes can be related to the temperature of operation, initial stoichiometry, or processing conditions. Typical structural changes of this type are seen as mixing of lithium and nickel (similar size), oxygen loss, or degradation of the surface layers to similar materials, including various defect spinel or rocksalt structures. In this section we are establishing the conditions required to convert a lithium-deficient NMC cathode material back to a stoichiometric material using low to mid ($< 400^\circ\text{C}$) temperature annealing in the presence of a lithium source, O_2 -containing atmosphere, and lithium source material. Re-lithiated materials will be characterized and studied for electrochemical activity, extent of anti-site mixing, and sample purity.

Results

Standard delithiated samples of composition $\text{Li}_{0.9}(\text{NiMnCo})\text{O}_2$ were created and supplied by Pupek and Dahl at the MERF facility from the baseline NMC111 provided by CAMP. While the overall composition of the cathode was determined by ICP to be the target composition, the issues associated with relithiation have been discussed for studies mainly related to LiCoO_2 .¹ Especially for thermally relithiated samples, the relithiation pathway used can create the correct stoichiometry but also induce anti-site cation

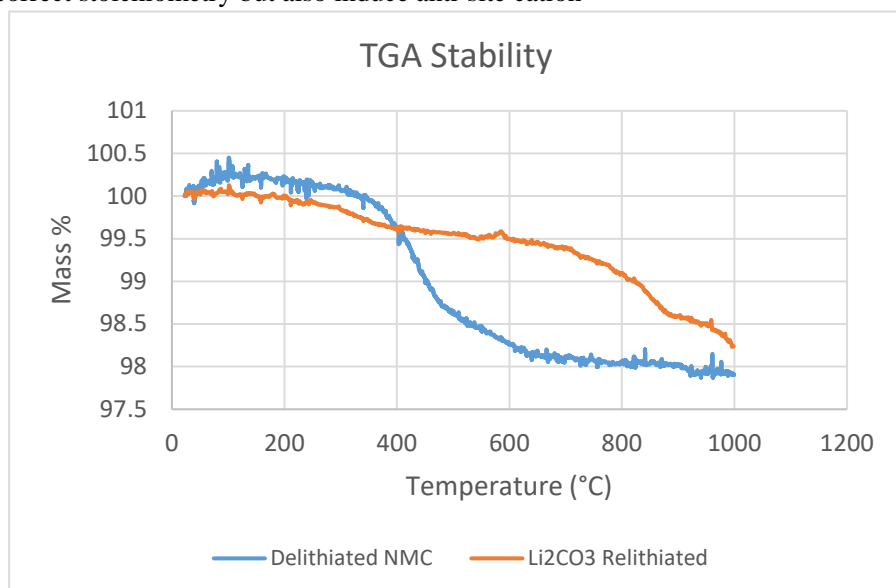


Figure 1. TGA curves for delithiated and relithiated NMC111 heated to 1000 °C under air atmosphere.

mixing, condensation from a layered to three-dimensional solid (i.e. layered to spinel, layered to rocksalt), or surface layers that impede lithium diffusion. We initially used thermal gravimetric analysis (TGA) in air to determine the relative temperature stability range of the delithiated cathode. Figure 1 compares the temperature vs weight response for the delithiated and re-lithiated (lithium source – lithium carbonate) stoichiometric samples. Initial evidence indicates at this level of delithiation, the samples have a similar stability window with no significant events until 300 C. Based on differences in composition and similarity of temperatures, the reduction of the oxidized form to final product is most likely tied to oxygen loss at this temperature. Beyond simple relithiation at elevated temperature, techniques that involve minimal cation movement should be evaluated in the temperature region below 300 C to minimize cation mobility and lattice stability.

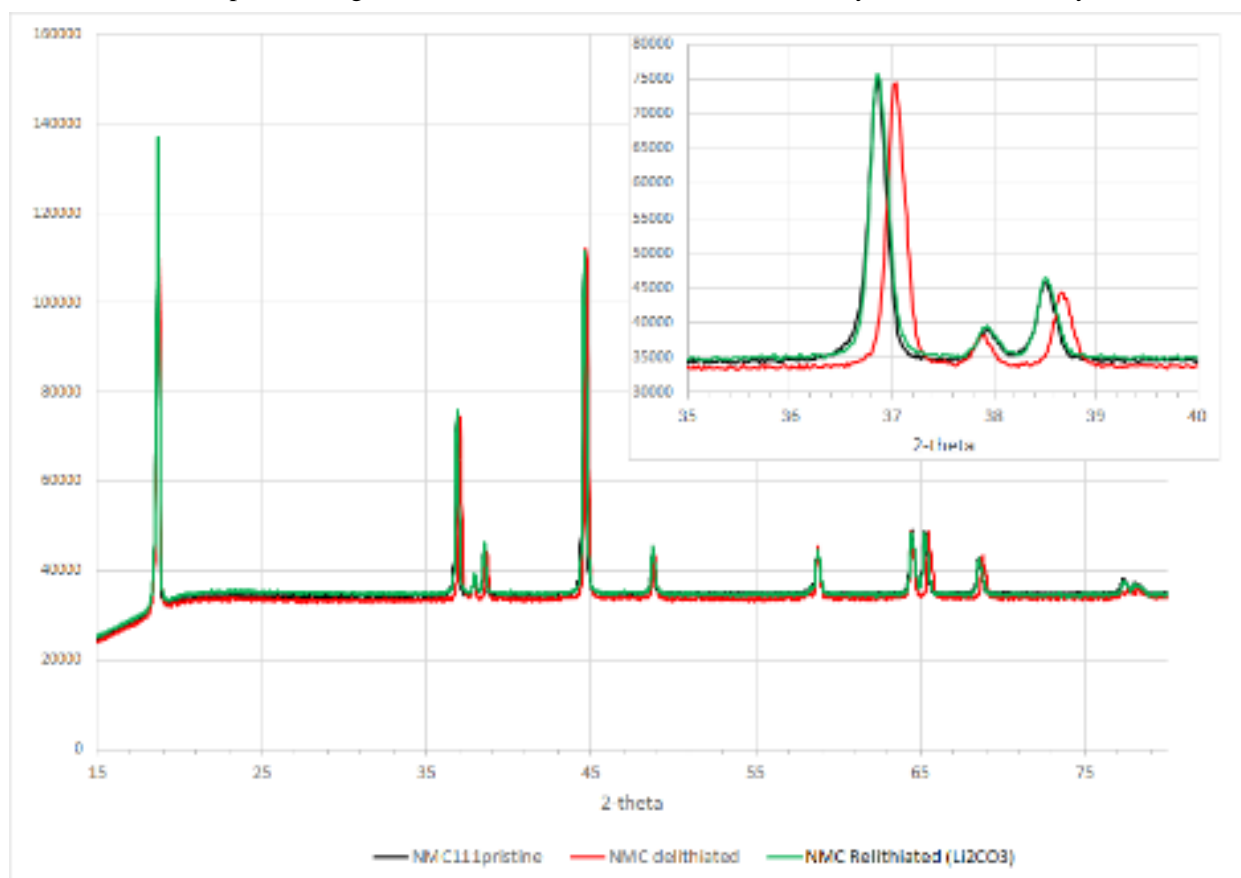


Figure 2. XRD overlays for pristine, delithiated, and relithiated NMC 111. Inset shows zoom in from 35-40 degrees

To create the relithiated product using heat treatments, relithiation reactions with delithiated NMC111 were done using a variety of common lithium salts, including $\text{LiOH} \cdot \text{H}_2\text{O}$, Li_2CO_3 , and LiOH . Salts were dissolved in water for 1 hour with constant stirring to a solution containing the cathode. Samples were then dried before annealing at 700 C for 18 h. Powder X-ray diffraction analysis of the pristine and delithiated NMC samples (see Figure 2) show distinct peak shifts indicative of the layers returning to their initial positions, and recreation of the pristine unit cell parameters. As noted above, the relithiation process can induce anti-site mixing as a side effect that adds impedance to the interfacial ionic transfer. From XRD analysis, the intensity ratio of the 003 and 104 peaks can qualitatively evaluate $\text{Li}^+/\text{Ni}^{2+}$ anti-site mixing, with a higher I_{003}/I_{104} ratio indicating less site mixing. Relithiated products were annealed at 500 °C to observe shifts in this intensity ratio.² Table 1 gives the calculated ratios from reactions with different lithium sources. A notable decrease was observed mainly for the delithiated NMC after annealing, in agreement with the hypothesis that in the absence of lithium in the layer, nickel cations could migrate under the influence of temperature. Samples with lithium filling the layer showed minimal changes to the ratio.

Future work will use GDOES (Glow Discharge Optical Emission Spectroscopy) to evaluate the homogeneity of the re-lithiation. This lithium-sensitive technique uses optical emission combined with depth profiling to yield information about sample homogeneity. Samples will be evaluated using electrochemical testing using standardized ReCell protocols to evaluate performance, passivation stability, and help identify surface dead layers that may be below XRD detection limits.

Table-1: X-ray diffraction peak intensity ratios for treated NMC111 materials.
Annealing performed at 500 °C under an air atmosphere.

	I_{003}/I_{104}	I_{003}/I_{104} (Post anneal)
Pristine NMC 111	1.29	1.27
Delithiated NMC 111	1.26	1.04
NMC Relithiated (LiOH H ₂ O)	1.20	1.13
NMC Relithiated (Li ₂ CO ₃)	1.33	1.35
NMC Relithiated (LiOH)	1.24	1.27

Conclusions

Initial work on thermal relithiation has identified that the delithiated lattice (15%) is stable to approximately 300 C. Effort to relithiate the lattice at higher temperatures, roughly recreating the initial synthesis conditions have been successful in restoring the lattice to full lithiation (XRD) with no significant anti-site mixing. Lower temperature methods, more in line with lattice stability measurements, and more active lithium sources are to be investigated as they may play a critical role in reducing costs.

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Electrochemical Relithiation

Jaclyn Coyle, Xuemin Li, Anthony Burrell (NREL)

Background

Recycling end-of-life (EoL) lithium-ion batteries (LIBs) is of great consequence as it provides a domestic supply of relevant transition metal materials and helps alleviate environmental pollution concerns associated with mining, long-distance transport, and landfill contamination. Similar worries in the Pb-acid battery industry have been alleviated to great extent by a successful recycling operation that helps close the loop on auto battery-derived lead in the environment. Conventional LIBs recycling methods including pyrometallurgy and hydrometallurgy processes have limitations of energy inefficiency, extensive gas treatment, complex chemical reaction and purification steps for leaching and separating metals. The objective of this project is to develop an electrochemically-based recycling and revitalization method for EoL battery cathodes. The EoL cathode performance and structure are to be recovered by electrochemical relithiation by using Li metal sacrificial anode, as Li ion (Li^+) inventory loss plays a significant role for the cathode degradation.

Results

1. Powder Characterization

The pristine and delithiated NMC powders were characterized using XRD, Raman, SEM, and FTIR in nitrogen atmosphere to compare their structural, morphological, and surface properties. From the results of XRD, Raman and SEM, no detectable structural and morphological difference can be observed. However, the TGA profiles show that the delithiated NMC 111 has higher mass loss at the temperature range of 300 – 600 °C. The higher mass loss percent of the delithiated NMC 111 is probably caused by the oxygen release when $\text{Ni}^{3+}/\text{Ni}^{4+}$ ions get reduced to Ni^{2+} upon heating [1] or by surface side reaction products such as LiCO_3 [2], which needs further characterizations to make a clear conclusion.

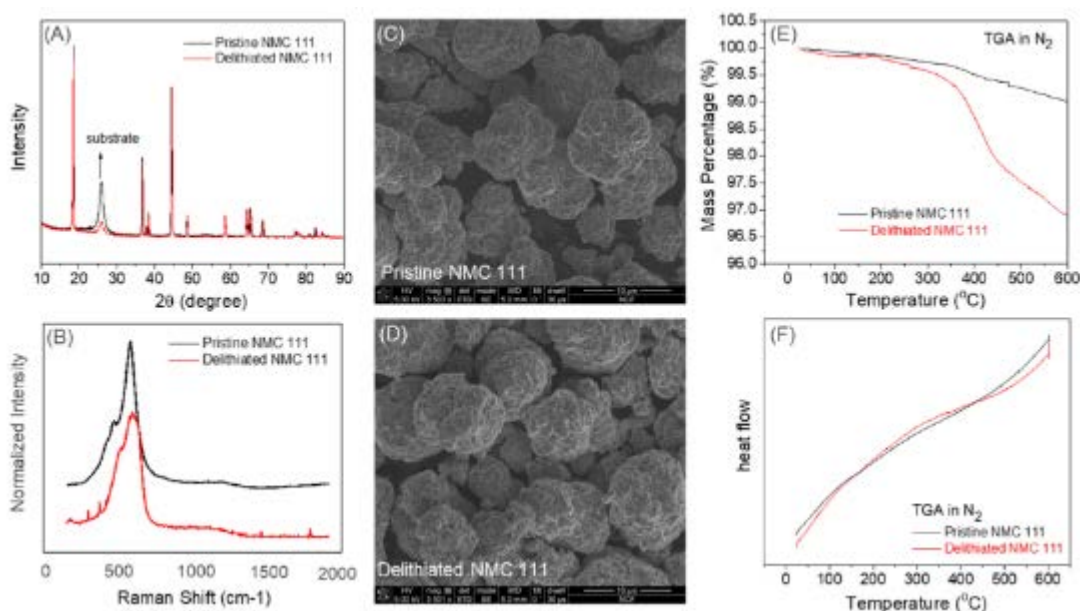


Figure 1. Characterization results of the pristine and delithiated NMC powders, with XRD (A), Raman (B), SEM (C) for pristine and (D) for delithiated NMC 111, and TGA from room temperature to 600 °C in N_2 atmosphere at the ramp rate of 5 °C/min in terms of mass percent (E) or heat flow (F) vs temperature.

2. Electrochemical Relithiation of Chemically Delithiated NMC 111

- a. The laminated cathodes using pristine and delithiated NMC powders were prepared with the composition of 90% NMC, 5% of PVDF, and 5% of conductive carbon. Then, the pristine and delithiated NMC cathodes were paired with Li metal in the coin cells for cycling at the voltage window of 2.8-4.2 V with the current rate of C/10. Table 1 includes the half-cell performance of the first 3 cycles. From the capacity results it can be seen that for the electrochemical relithiation into the Li⁺ deficient NMC 111, starting from cell discharging, i.e. lithiation for the delithiated NMC, the cell average capacity is slightly higher than that starting from cell charging. Therefore, we always initially discharge the delithiated NMC laminated cathodes shipped from CAMP in the next step.
- b. After we received the CAMP laminated cathodes of pristine and delithiated NMC 111, we assembled half coin cells using the delithiated NMC 111 starting from discharging the half cells to 2.8 V, then cycled the half cells for another 2 times between 2.8 – 4.2 V. The results are included in Table 2. After relithiation in half cells, the relithiated NMC 111 electrodes were extracted from the half cells in the Ar-filled glove box using a Hohsen coin cell disassembler. Then they were rinsed using DMC solvents for full cell reassembly in pair with the pristine graphite anode shipped from CAMP. As the pristine graphite anode was not formed, when pairing with the relithiated NMC 111, the cell OCV is ~ 0.5 V. Li⁺ ions in the relithiated NMC are consumed again during the first several cycles due to SEI formation on graphite anodes. The capacity results of the reassembled cell together with that of pristine cathode/pristine anode are also included in Table 2. It can be seen that the reassembled full cells did not show better or identical performance as that of the pristine electrodes due to the anode formation process. Therefore, we plan to use pristine but formed graphite anodes for the future studies.

Table-1: The first 3 cycle capacity values for pristine and chemically delithiated NMC 111 powders in half cells. The current rate is C/10 between 2.8 V and 4.2 V.

Materials	Delithiated – Cycle from discharging		Delithiated – Cycle from charging		Pristine	
	Chg (mAh/g)	Dchg (mAh/g)	Chg (mAh/g)	Dchg (mAh/g)	Chg (mAh/g)	Dchg (mAh/g)
The avg 1 st cycle		4.46	123.07	133.45	147.74	130.52
The avg 2 nd cycle	129.88	137.51	135.12	134.64	131.26	131.66
The avg 3 rd cycle	138.09	138.11	135.01	134.73	132.04	132.16

3. Plan for relithiation conditions
 - a. Study the effect of lower cutoff voltages such as 2.8 V, 2.3 V, and 1.8 V for electrochemical relithiation.
 - b. Study the effect of temperatures and current rates for electrochemical relithiation to find out an economic strategy.
 - c. Find out a cheaper electrolyte for the electrochemical relithiation.
 - d. Decaying the full coin cells and pouch cells to get electrochemical delithiated NMC 111 for future electrochemical relithiation study.

Table-2: The relithiation capacities of the chemically delithiated NMC 111 laminated cathodes in half cells, reassembled full cell capacities with relithiated NMC vs pristine graphite, and full cell capacities with pristine NMC and graphite. The current rate is C/10 between 2.8 V and 4.2 V.

Materials	Half cell for relithiation Delithiated NMC 111 vs. Li		Reassemble into full cell Relithiated NMC vs pristine graphite		Full cell Pristine NMC vs pristine graphite	
	Chg (mAh/g)	Dchg (mAh/g)	Chg (mAh/g)	Dchg (mAh/g)	Chg (mAh/g)	Dchg (mAh/g)
The avg 1 st cycle		3.379	144.56	119.78	136.06	110.22
The avg 2 nd cycle	128.79	134.64			122.44	120.91
The avg 3 rd cycle	135.48	135.23			125.37	124.79

Conclusions

The morphology, composition and structure of the initial NMC 111 pristine and chemically delithiated powders used for the ReCell project were characterized through Raman spectroscopy, FIB SEM and TGA. These initial powders were determined to be very close in morphology and structure. These analysis techniques will continue to be utilized during examination of prolonged cycling for both pristine and relithiated NMC 111 cathodes in order to determine the success of electrochemical relithiation procedures. Initial electrochemical results on laminated electrodes synthesized at NREL show that an initial discharge procedure is more effective for relithiation. Cells rebuilt after relithiation using electrodes provided by the CAMP facility provided evidence that the anode used for rebuilt cells should be pre-formed as well to allow for optimal capacity.

References

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Ionothermal Relithiation

Sheng Dai, Huimin Luo, Nitin Muralidharan, Jianlin Li, Zhijia Du, and Ilias Belharouak (ORNL)

Background

Our project is focused on developing low-cost process to relithiate and/or upgrade used cathode at ambient pressure based on ionic liquids. Ionic liquids (ILs) are a family of non-conventional molten salts that offer many advantages, such as negligible vapor pressures, negligible flammability, wide liquidus ranges, good thermal stability, and much synthesis flexibility. The unique solvation environment of these ionic liquids provides new reaction or flux media for controlling formation of solid-state materials with a minimum perturbation of morphologies¹. The ionic liquid can be readily recycled through this ionothermal lithiation.

Results

During the first two quarters, three ionic liquids $[C_2mim][NTf_2]$, $[C_4mim][NTf_2]$, and $[C_2OHmim][NTf_2]$ have been synthesized and characterized. The synthesis scheme and the structure of anion are shown in Figure 1. Ionothermal lithiation experiments in these ionic liquids have been performed following modified literature procedures². Typical procedure is as following, stoichiometric amounts of delithiated-NMC111 (~2.5 mmol) and LiCl (~2.5 mmol) or other lithiated agent were mixed in ILs (~2.5 mL) in a 50 mL glass vial. After vibrating 10 minutes, the vial containing the mixtures was heated in a heating block up to 250°C within ~40 min and kept at 250°C for another 24 hours. After the mixture cooled down to room temperature, the cathode was separated from ionic liquid by centrifugation. The recovered cathode was washed with acetone, DI H₂O twice, and finally with acetone. The cathode was dried in vacuum oven at ~100°C for ~18 hours. The obtained powder or cathode was characterized by X-ray diffraction (XRD) and thermal gravimetric analysis (TGA).

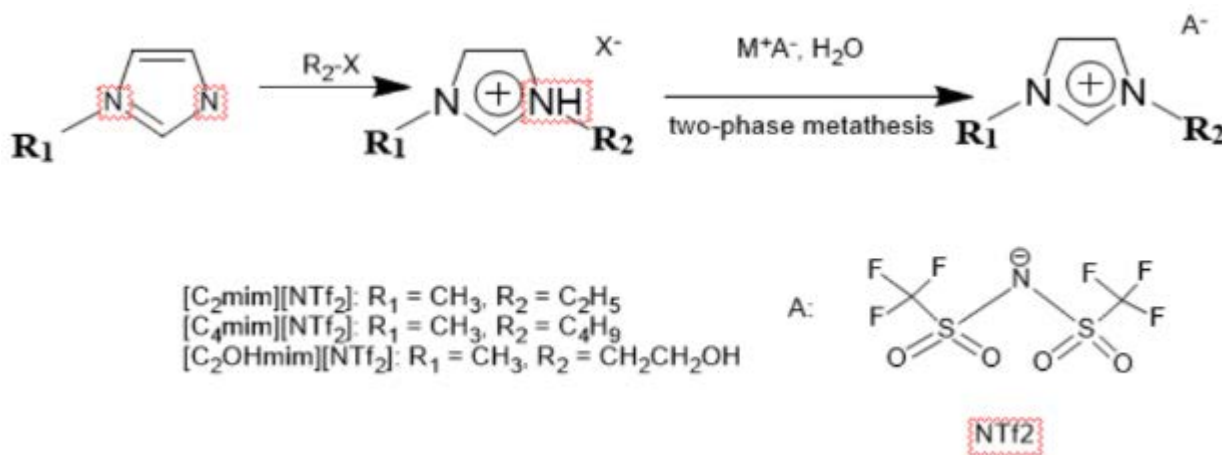


Figure 1. Synthesis scheme of ionic liquids and the structure of NTf₂ anion

From Figure 2, XRD patterns show that the peak splitting of (108) and (110) in the crystal structure of cathode after ionothermal lithiation with LiCl or LiOAc in ionic liquids both narrowed after lithiation reaction indicating Li restoring to some degree according to literature³.

Delithiated-NMC111 and pristine NMC111 were received from Argonne and analyzed by TGA as received and after dried under vacuum at $\sim 100^{\circ}\text{C}$ for 3 days. TGA plots (Figure 3) did not show any difference indicating that the delithiated-NMC111 can be used as received without further drying. Results of ionothermal experiments in ILs at three different temperatures are summarized in Table 1.

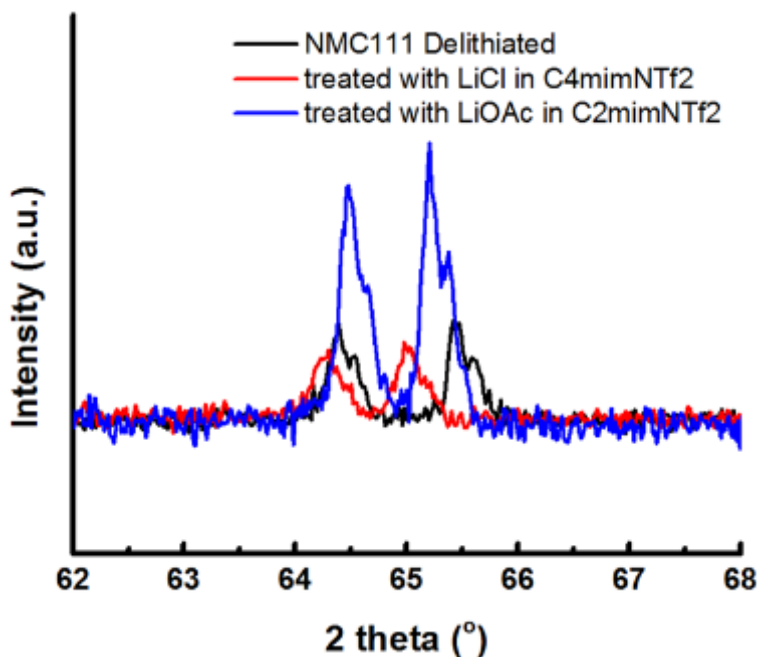


Figure 2. Comparison of XRD plots of black mass recovered with NMC111-delithiated as received

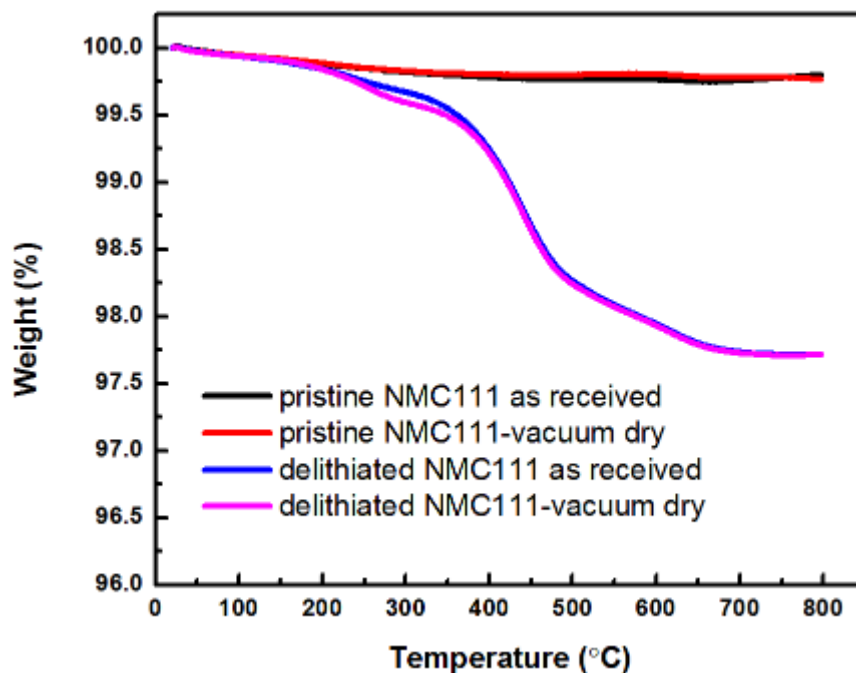


Figure 3. TGA plots of NMC111-delithiated and pristine NMC111

Two lower experiment temperatures (225°C and 200°C) besides literature temperature (250°C) were used in ionothermal experiments this quarter. It seems that ionic liquids can be recovered from 73% to 93% depending on which reagent and ionic liquid are used. LiCl gave a better recovery of IL than LiOAc when [C₂mim][NTf₂] was used. Cathode recovery ranged from 78% to 96% depending on temperatures, agents and ionic liquids. Based on TGA results (Figure 4), when LiCl was used in IL containing a hydroxy group (-OH) at 200°C gave the best result so far since their TGA final weight percentage is 99%, which is the closest to TGA plot of pristine NMC111 (left plots of Fig. 4), however, still waiting for the confirmation of XRD results. TGA plots also indicate that lower temperature gave better thermal stability for the cathode recovered when same IL was used (right plots of Fig. 4).

Table 1. Summary of ionothermal experiments and TGA final weight percentages of cathode recovered

Ionic liquid	Lithiated reagent	Temp.	Cathode recovered (%)	IL recovered (%)	TGA final (%)
[C ₂ mim][NTf ₂]	LiCl	250°C	22.8	92.0	97.73
	LiOAc	250°C	89.0	76.9	98.56
	LiCl	200°C	95.7	93.2	98.32
	LiOAc	225°C	81.7	73.0	98.17
[C ₄ mim][NTf ₂]	LiCl	250°C		Need to repeat	
	LiCl	225°C	93.0	92.5	98.55
[C ₂ OHmim][NTf ₂]	LiCl	250°C	78.4	90.4	96.76
	LiCl	200°C	82.8	92.7	99.06
Pristine NMC111	As received				99.80
	Vacuum dried				99.80
Delithiated NMC111	As received				97.84
	Vacuum dried				97.72

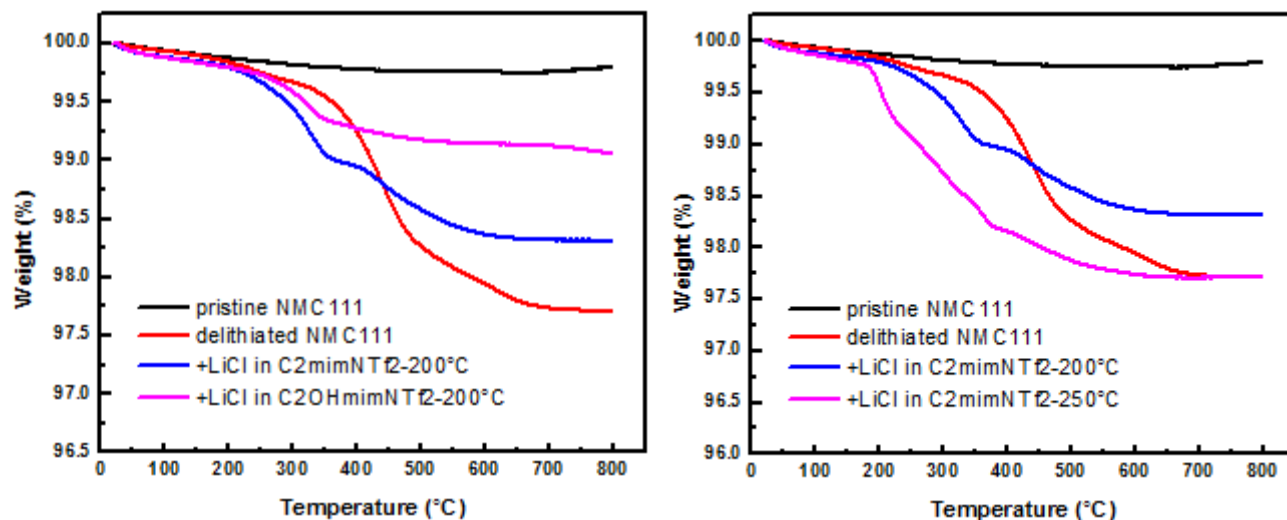


Figure 4. TGA plots of lithiated with LiCl at two different temperatures (right) and in two different ILs (left)

Conclusions

In summary, during the first two quarters, three new ionic liquids have been synthesized. Ionothermal experiments at different conditions have been performed. The recovered cathode has been characterized by XRD and TGA. Based on our preliminary results from these two first quarters, we believe that our ionothermal approaches towards restoring Li into delithiated NMC111 for Li-ion battery recycling are promising and feasible. Optimizations of process parameters such as temperatures, time, ionic liquids and Li-reagent will be further investigated in the next few quarters.

Milestones and Deliverables

- Task 1 (M1-3):** Screen and develop ionic liquids to restore aged cathode materials via ionothermal lithiation.
Task 2 (M3-6): Relithiate NMC111-delithiated in selected ionic liquids at different ionothermal conditions

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Hydrothermal Relithiation

Zheng Chen (UC San Diego)

Background

Lithium-ion batteries (LIBs) have been widely used in mobile electronics, electric vehicles (EVs) and renewable grids due to their high energy density.¹ Typical LIBs reach their end of life (EoL) after a few years of service due to performance degradation. It is projected that ~1 million tons of used LIBs will be taken out of the market by 2025.²⁻⁴ From the economic point of view, re-use of the constituent precious metals (e.g. \$60/kg for Co, \$15/kg for Ni, \$20/kg for Li)⁵ from LIBs can significantly reduce their cost because a significant portion (30-40%) of the LIB cost comes from their cathode materials.⁶ From the environmental point of view, the flammable and toxic wastes (organic solvents, heavy metals) generated from disposal of used batteries can be the cause severe environmental pollution.⁷ Therefore, it is important to recycle, reuse and re-manufacture LIBs to create a sustainable energy storage system.⁸ The state-of-the-art approach to recycle cathode materials is mainly a hydrometallurgical process which involves acid dissolution followed by chemical precipitation.⁹⁻¹² However, large amounts of acid and base solutions are used, which generate additional waste and complicates the recycling process. More importantly, the embedded energy used to initially create desired cathode particles is lost during such a destructive recycling process. With this in mind, there is a growing interest on the direct recycling of cathode materials with retention of structure, such as a solid-state sintering approach, in which a pre-determined amount of lithium salt (e.g., Li_2CO_3) is mixed and sintered with the spent cathode powders to generate new particles.^{7, 13, 14} This relatively green approach simplifies the recycling process and retains the embedded energy, however, only LiCoO_2 (LCO)^{7, 13} and LiFePO_4 ¹⁴ cathode materials have been investigated. Due to the high capacity and reduced cost, layered oxide $\text{LiNi}_x\text{Co}_y\text{Mn}_z\text{O}_2$ ($0 < x, y, z < 1$, $x+y+z=1$) or NMC is becoming the dominating cathode material in the state-of-the-art LIBs.¹⁵ So far, the recycling of NMC cathodes has been mainly based on the hydrometallurgical process as mentioned earlier.^{4, 16-20} Therefore, there is an acknowledged need to develop an energy-efficient, non-destructive process to directly recycle NMC cathodes. One promising approach is to combine hydrothermal relithiation with appropriate post-treatment (e.g., thermal annealing) to perform direct cathode recycling. An issue associated with the direct relithiation by addition of a lithium salt and annealing is that cathode stability and homogeneity may change with their original composition and crystal structure which can influence electrochemical cycling. This has been most studied for LCO and similar systems with partial delithiated host materials sometimes in equilibrium with transformed phases (i.e. Co_3O_4) as stable delithiated species²²⁻²⁹. These complicated degradation mechanisms suggest that a fundamental and systematic study on the composition and phase change upon direct regeneration is needed. The current project is focused on understanding hydrothermal relithiation processes for NMC cathodes, with an initial focus on chemically delithiated NMC111.

Results

The first step to directly regenerate the degraded cathode particles is to re-dose lithium using a hydrothermal-based solution impregnation method. Hydrothermal relithiation was first performed on chemically delithiated NMC111 cathodes (provided by the Materials Engineering Research Facility at Argonne) and the composition of different cathode particles was quantified using inductively coupled plasma mass spectrometry (ICP-MS) measurement. **Figure 1** illustrates the lithiation process of the NMC111 cathode particles during the hydrothermal treatment at different temperature (200 and 220 °C). It is found that chemically delithiated NMC111 particles can reach >1.05 Li (per transition metal or TM) in about 1 hr, which is approximately the same ratio as the pristine NMC111 sample. However, it is interesting to note that as the treatment time increases, the Li ratio decreases and then increases again from 1 hr to 6 hr. Overall, the 1hr sample shows the highest Li ratio among all the samples. This behavior remains to be further understood (possible reason might be the proton replacement or surface Li adsorption).

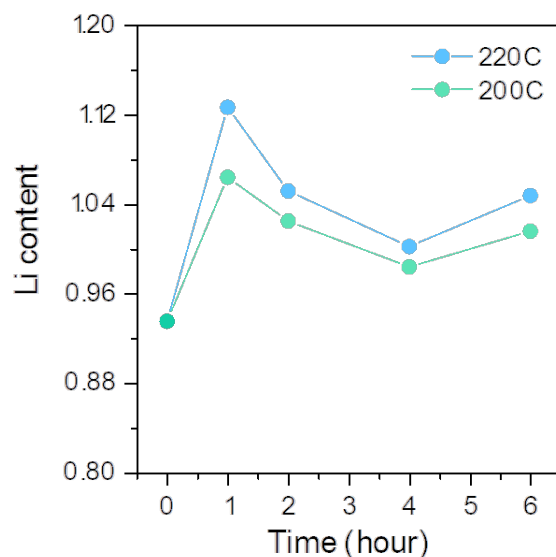


Figure 1. Lithiation kinetics of chemically delithiated Toda NMC111 at 200 and 220 °C in 4M LiOH solution.

It is also critical to investigate the evolution of the microstructure defects. The X-ray diffraction (XRD) patterns of pristine, chemically delithiated and hydrothermal relithiated cathode particles are shown in **Figure 2**. The chemically delithiated cathode particles show a high relative intensity ratio of I_{003}/I_{104} (1.39), suggesting higher cation mixing, which is consistent with previous report.²² The (003) peak shifts to lower angles, corresponding to an increase in c lattice parameter due to the electrostatic repulsion between the oxygen layers along c directions in the Li deficiency state.³⁰ The spacing between the peaks in the (108)/(110) doublets increases after chemical delithiation, corresponding to the decrease in a lattice parameters due to the smaller effective ionic radii of Ni^{3+} than Ni^{2+} to compensate Li deficiency.³¹ After different relithiation time, the (003) peak shifts back towards higher angles and the spacing between two doublets peaks decreases, which indicates the recovery of the pristine crystal structure.

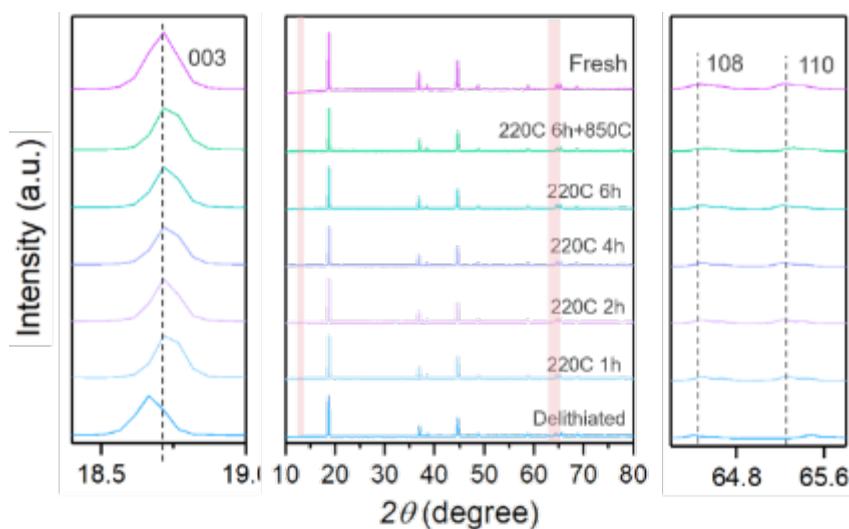


Figure 2. XRD patterns of fresh, chemically delithiated (0 hr) and hydrothermal treated Toda NMC111.

The electrochemical performance of NMC111 cathode particles obtained in different conditions were evaluated by making coin cells (half-cell) with cathode mass loading of $\sim 10 \text{ mg cm}^{-2}$. The electrolyte was LP40 (1M LiPF_6 in EC/DEC) and cells were cycled in the voltage range of 3–4.3 V at 0.1C ($C = 150 \text{ mA g}^{-1}$) to evaluate their electrochemical activity (**Figure 3**). As the reference, the pristine cathode shows a capacity of 182 and 152 mAh g^{-1} for charge and discharge, respectively. While the 1hr treated sample has the highest Li ratio, its capacity is lowest (177 and 149 mAh g^{-1} for charge and discharge, respectively). As the hydrothermal time increases, the discharge capacity increases, reaching a maximum value of 156 mAh g^{-1} for 6hr treated sample. All the samples show similar charging capacity, which may suggest the layer structure of the NMC111 samples were well retained during the chemical delithiation and hydrothermal treatment processes, which maintain the active sites for electrochemical reaction. More electrochemical test is undergoing with changing the hydrothermal conditions as well as combining with post-annealing treatment on the relithiated cathodes samples.

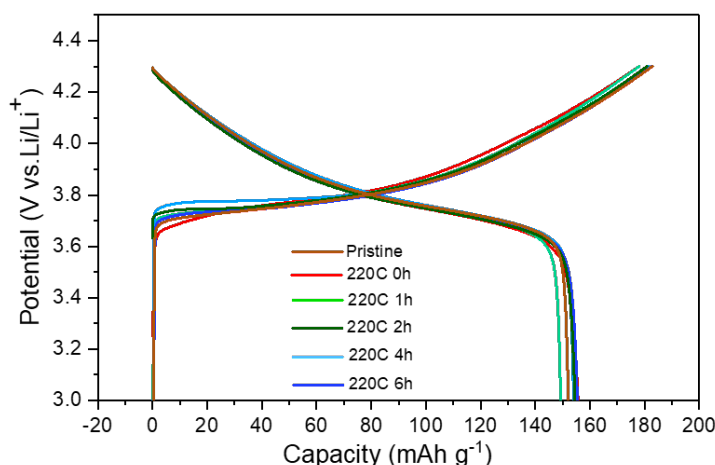


Figure 3. Galvanostatic charge/discharge curves of pristine, chemically delithiated (0hr) and hydrothermal treated Toda NMC111 cathode samples.

Conclusions

In summary, hydrothermal relithiation of chemically delithiated NMC111 was performed with systematical characterization of the chemical compositions and crystal structures of different samples. The results suggest that desired Li ratio can be achieved with well-maintained layered structures. The electrochemical activity of the relithiated NMC111 can also reach the same level of pristine samples. However, it remains to study the correlation between the Li composition and the electrochemical performance as there is no clear trend. Also, the hydrothermal kinetics does not reflect a typical kinetics trend, which also needs further investigation.

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Binder Removal

Albert L. Lipson, Bradley Ross (Argonne)

Background

Once cathode materials are separated to be recycled, the poly(vinylidene difluoride) (PVDF) binder needs to be removed to allow for further processing. This can be done using a large quantity of n-methyl-2-pyrrolidone (NMP), but this is not cost effective for battery recycling. Other methods need to be explored in order to enable profitable direct cathode recycling, such as thermal decomposition and mechanical methods. Both these methods require substantial development to allow for them to remove PVDF without damaging the cathode material. Thermal decomposition can result in substantial fluorine doping of the cathode material, thereby increasing impedance and reducing capacity. Various methods to prevent fluorine doping into the cathode material need to be developed, such as adding materials to absorb fluorine or create a fluorinated coating. Mechanical methods require a careful balancing to prevent cracking of the cathode while removing the binder, which could be made simpler by going to lower temperatures to embrittle the PVDF.

Results

In order to understand how PVDF decomposes in contact with $\text{LiNi}_{0.333}\text{Co}_{0.333}\text{Mn}_{0.333}\text{O}_2$ (NMC 111) thermogravimetric analysis (TGA) with mass spectroscopy (MS) detection of the gasses was utilized (Figure 1). From this data we see that PVDF begins to decompose at about 350°C in air. The decomposition of PVDF completes at around 500°C. Meanwhile, the carbon black decomposes between 450°C and 500°C. At temperatures above 900°C fluorine is released from the NMC or crucible walls along with Li from the cathode. This data indicates that both carbon black and binder will be nearly completely decomposed at 500°C, and this is the temperature that was selected for our initial studies. It is also possible that PVDF could more slowly decompose and thereby reduce the amount of doping by holding at lower temperatures for longer periods of time.

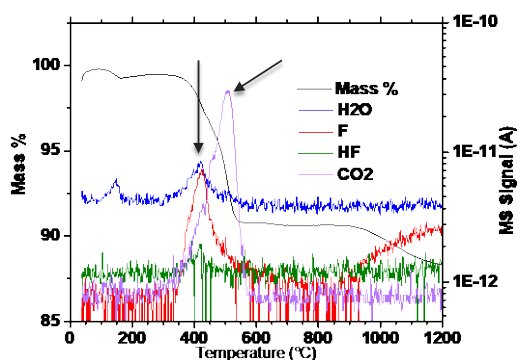


Figure 1. TGA-MS at 5°C/min of broken up laminate containing 90 wt.% NMC 111, 5 wt.% PVDF, and 5 wt.% carbon black.

To see what effect this decomposition has on the electrochemistry of NMC 111, the material with different amounts of binder and 2 different heat treatment profiles were tested (Figure 2). Using the faster furnace profile, capacities at all PVDF amounts are substantially reduced. Additionally, the rate performance is hindered. Using the slower ramp rate, capacities are improved with the 1 wt.% PVDF sample nearly matching the pristine in performance. This data coupled with the TGA-MS indicate that slower ramping and a hold at lower temperature may more effectively remove PVDF without doping the NMC.

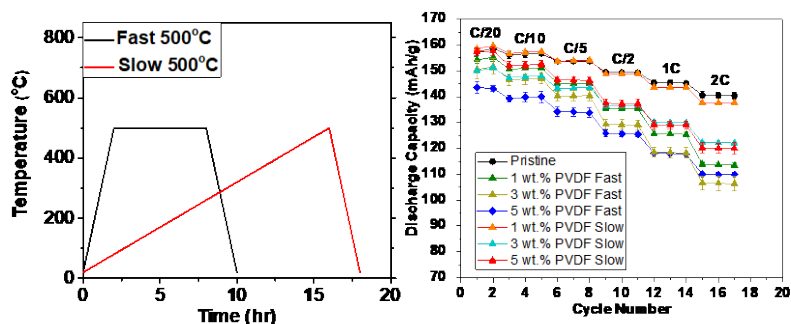


Figure 2. Furnace heating profiles (left). Electrochemical performance with different amounts of PVDF and 5 wt.% carbon black, broken up, heat treated, and then remade into electrodes with 5 wt.% PVDF and 5 wt.% carbon black (right).

Different additives to the process were also explored to try to either capture fluorine or create a fluorinated coating on the cathode surface. Figure 3 shows the results from two of these experiments. The first is utilizing nanoporous alumina or silica particles that were sieved to be greater than 45 μm for easy removal after the heat treatment. The nanoporous alumina shows a minor improvement in rate performance and silica hinders performance. Other weight percentages of alumina were tried with no further benefit. These additives suffered from poor contact with the PVDF and therefore did not pick up enough fluorine to improve performance. To remedy this both nanoparticle alumina and an aluminum containing precursor (aluminum acetoacetate ($\text{Al}(\text{acac})_3$)) were added before the heat treatment. Nanoparticle alumina showed no improvement, but adding 1 wt.% $\text{Al}(\text{acac})_3$ did show some improvement in rate performance at the cost of initial capacity. Both higher and lower amount of $\text{Al}(\text{acac})_3$ made things worse. So far, none of the additives tried improved performance significantly.

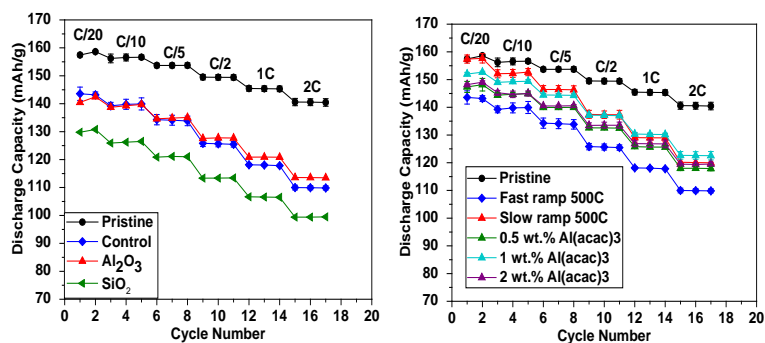


Figure 3. Electrochemical rate performance of materials after fast (left) or slow (right) heat treatment. The additives were acoustically mixed with the broken up laminate with 5 wt.% binder before heat treatment.

Conclusions

Initial studies of the thermal decomposition of PVDF binder demonstrate the difficulty in implementing an efficient process. Capacity and rate performance are significantly reduced, which is likely caused by fluorine doping into the NMC structure. Additives that should mitigate the effects of fluorine have not significantly improved the capacity or rate performance. However, changing the furnace heating rates seems to improve the performance of the material after thermal decomposition. This along with the TGA-MS results indicate that holds at temperatures between 350°C and 400°C might further increase performance after heat treatment.

Cathode/Cathode Separation

Erik Dahl, Alison Dunlop (Argonne)

Background

For a commercial LIB recycling operation, the expected materials recovered will represent a mixture of the cathode materials used in the marketplace over the previous decade. Even if cells are presorted before processing, it is still highly likely that some mismatch will occur. Since each cathode may have a specific regeneration process, different elemental constituents, or reactivity, the ability to separate these mixed cathode streams by chemistry represents an important barrier to commercially viable cathode recycling. In practice most direct recycle pre-processing operations involve the collection of a “black mass”, a mixture of anode (typically graphitic carbon) and cathode powders recovered from shredded cells. After anode/cathode separation, the various cathode powders can be isolated and processes developed. As direct recycling is projected to be the least energy intensive, a method to separate the cathode waste streams is critical to improve the economics of lithium-ion battery recycling while reducing dependence on imported raw materials.

Results

Before processes can be defined to relithiate recovered cathode materials, a standard baseline material for use by researchers in the program was created using a chemical delithiation process. Using a commercial NMC111 sample we used a literature method to delithiate (oxidize) the sample using an ammonium persulfate ((NH₄)₂S₂O₈) solution, that mimics a voltage ~5V (vs Li). The method was scaled up to 2kg batch size and yielded a final stoichiometry (ICP) of Li_{0.85}(Ni_{0.33}Mn_{0.33}Co_{0.33})O₂ that was distributed to the teams.

Samples were tested for electrochemical activity as well to confirm the process did not damage the material or act as a second evaluation of the post-processing lithium content. As noted in Table 1, the delithiation process used for the scale up had no effect on the electrochemical activity of the materials. The drop in measured capacity for the delithiated material reflects the lithium loss during the processing and is in line with the lithium content from the ICP analysis. The stability of the electrochemical cycling on further cycling also supports the observation that no noticeable damage to the host lattice was done. Future work being scaled up at AMD Division will be to develop a process to create a delithiated sample with a more significant delithiation. Such materials, with as much as 50% of the lithium removed, would be useful models for end of life stability measurements, role of more highly oxidized cathodes in the processes used, and possible ways to detect oxygen non-stoichiometry as a failure mechanism.

Table-1: Comparison of NMC111 Before and After Delithiation

Cathode	NMC 111 Pristine (4cells)	NMC 111 Delithiated (2cells)
Cycle 1 Charge	175 mAh/g	153 mAh/g
Cycle 1 Discharge	153 mAh/g	160 mAh/g
1 st Cycle Efficiency	88%	104%
3 rd Cycle Charge	155 mAh/g	161 mAh//g
3 rd Cycle Discharge	153 mAh/g	160 mAh/g

In addition to supplying a delithiated baseline for research groups in the program, we have been establishing the feasibility of using magnetic separation of mixed cathode materials. As many of these oxides are magnetic, the differences in magnetic properties may be significant enough to allow this property to be used to separate

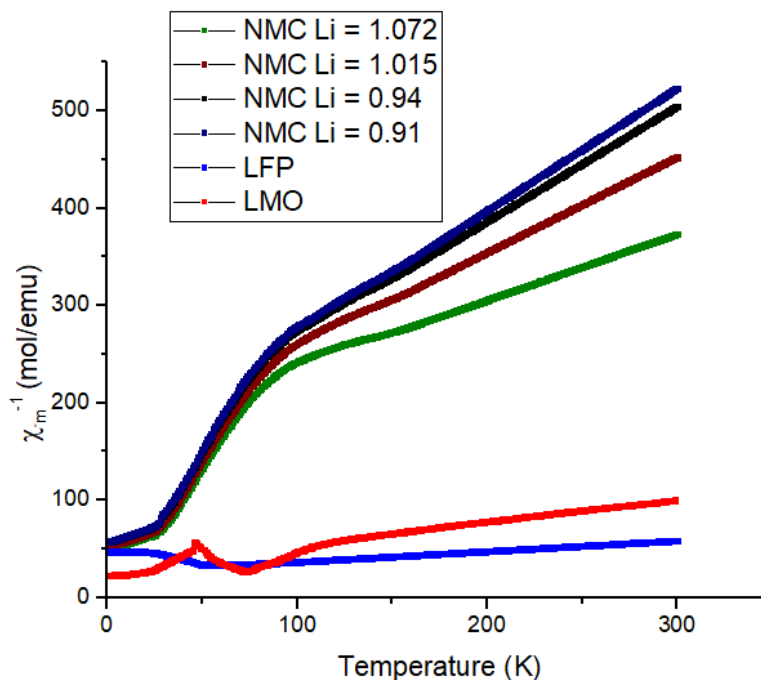


Figure 1. Magnetic susceptibility of various common cathode materials

or assist in separating the constituent oxides. In Figure 1, the susceptibility of relevant cathodes including various partially delithiated Toda111 samples, LiFePO_4 olivine, and spinel LiMn_2O_4 are shown as susceptibility versus temperature. In this figure, significant differences in magnetic susceptibility especially near room temperature are noted and investigations are underway to establish if it can be used in the separation process.

Conclusions

We have successfully scaled up the baseline delithiated cathode materials for the recycling effort in association with CAMP and MERF facilities. The delithiation process was found to have no effect on the electrochemical performance of the cathode, but for the lower first cycle capacity. The material was distributed as needed for team researchers. We are also started to evaluate the opportunity to use differences in magnetic properties of these cathodes to separate not only ones with different constituent metals but ones with different lithium contents. Preliminary evaluation shows significant differences are achieved and are being evaluated as a separation tool.

Cathode/Cathode Separation via Froth Flotation

Lei Pan, Tinu Folayan, Ruiting Zhan (MTU)

Background

Unlike other recycling processes, direct recycling requires single battery chemistries or compatible chemistries to be successful in the marketplace. With this, a need exists to be able to separate cathode chemistries from one another that may occur in a typical LIB waste stream. Direct cathode recycling provides the opportunity to obtain higher value recycling products. The success of this project is a critical piece to make direct recycling a reality. The purpose of this work is to investigate the effectiveness of froth flotation to separate different battery cathode chemistries in powder form. Our initial effort (Task 1) will be focused on producing a library describing the hydrophobicity/hydrophilicity for the cathode chemistries using different collectors. Cathode chemistries to include are LCO, LMO, LFP, NCA, NMC111, and NMC811.

Results

During this reporting period, we have conducted a series of froth flotation experiments to first evaluate the hydrophobicity for individual cathode chemistries without any chemical additives, and the result is shown in Table-1. In these experiments, 5-10 grams of cathode powders were added in 2 liter of de-ionized water with an addition of 10-20 μ L of methyl isobutyl carbinol (MIBC) as frother. The pH of the slurry was recorded. The recovery is the percentage of recovered materials in froth layer after 3 minutes flotation time. It was found that the recovery for lithium iron phosphate (LFP) is 100%, while that for other cathode chemistries were below 10%. The result suggests that the LFP is hydrophobic, while other cathode chemistries are hydrophilic. The hydrophobicity of LFP powders is attributed to carbon coatings on surfaces.

Table-1: Floatability of individual cathode active materials in de-ionize water at natural pH.

Cathode	Natural pH	Recovery (%)
NMC 111	8.28	9%
NMC 811	10.48	<2%
LFP	10.50	100%
NCA	10.50	<2%
LMO	7.40	6%
D-NMC 111*	6.80	<2%

*de-lithiated

The result in Table-1 suggests that the separation of LFP from other cathode chemistries is feasibility. However, the separation of other cathode chemistries, *e.g.*, the separation of NMC111 from LMO is not possible without controlling surface hydrophobicities of cathode chemistries. Selectively controlling the hydrophobicity of various cathode chemistries is critical to achieve separation via froth flotation technique. In the follow-up experiments, we have surveyed a number of chemical additives that selectively render one cathode chemistry hydrophobic. Table-2 shows the froth flotation separation result of individual cathode chemistries using different collectors at different pHs. The preliminary result shows that both hydroxamate and fatty acid work effectively in rendering NMC 111 and NMC 811 hydrophobic. It was also found that NCA is hydrophilic at pH = 6

regardless of types of collectors used. The result suggests that both hydroxamate and fatty acid might be the candidate for separation of individual cathode chemistries.

Table-2: Floatability of individual cathode active materials using different collectors.

Condition		D-NMC 111	NMC 111	NMC 811	LMO	NCA
Collector	pH					
Salicylaidixime	Natural	18%	80%	0%	72%	16%
Salicylaidixime	6	-	76%	18%	86%	0%
Cupferron	Natural	22%	34%	16%	38%	20%
Cupferron	6	<2%	60%	46%	43%	0%
Hydroxamate	Natural	95%	93%	96%	68%	68%
Hydroxamate	6	-	96%	91%	63%	0%
Fatty acid	Natural	100%	100%	98%	63%	82%
Fatty acid	6	-	99%	100%	96%	0%
Phenylthiourea	Natural	56%	33%	67%	40%	35%
Phenylthiourea	6	-	37%	27%	47%	0%

Figure 1 shows the result on the recovery of various cathode chemistries at different pHs when using fatty acid as the collector. It was found that the NMC 811 had a recovery of above 90%, and the recovery was not affected by pH in the range of 6-11. However, the recovery for LMO was found to be decreased significantly with increasing pH. On the contrary, the recovery of NCA was found to increase with increasing pH. At pH = 5, the recovery for NCA was nearly zero, while the recovery of NCA was above 90% at pH 10.8. The present result suggests that the separation of NMC and NCA might be achieved at pH = 6. However, the underlying mechanism is not clear, requiring more studies in the follow-up months.

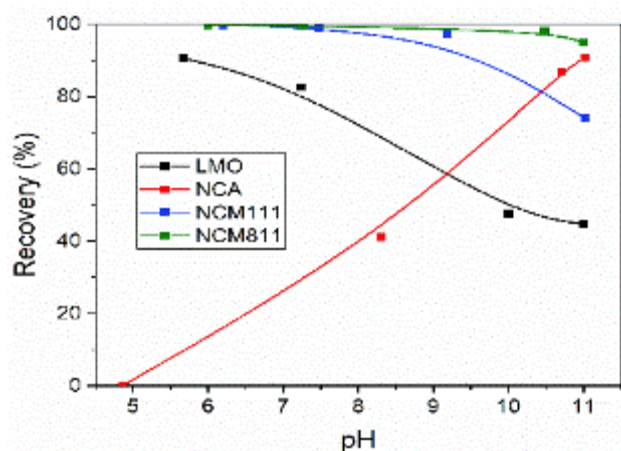


Figure 1. Effect of pH on floatability of individual cathode materials using fatty acid as the collector.

In addition, we have conducted anode/cathode separation by froth flotation technique. The feed is a mixture of pristine NMC111 and graphite supplied by Argonne. The froth flotation separation experiments were conducted in 2L Denver cells using the modified released analysis protocol. A total of five samples were obtained and sent to Argonne for electrochemistry evaluation. The thermogravimetric analysis (TGA) result shows the purity of produced anode materials is as high as 99.93%, while the purity of cathode materials is as high as 99.5%.

Conclusions

1. LFP is naturally hydrophobic, while other cathode chemistries are hydrophilic. Separation of LFP from other cathode chemistries is feasible, and this hypothesis will be tested in Q3.
2. A number of collectors were surveyed during this reporting period. Both hydroxamate and fatty acid were found to be effective collectors for various cathode materials.
3. The floatability of different cathode chemistries is dependent on pH. However, the underlying mechanism is still unknown.

Role of Impurities in Recycled Cathodes

Yan Wang (WPI)

Background

When identifying and developing lithium ion battery recycling technologies, understanding the role of impurities is always a concern as they may have an impact on electrochemical performance, material stability, or lifetime. While elemental doping is considered one of the most efficient ways to improve the electrochemical properties of cathode materials, the role impurities play concerning the final properties of precursor and cathode recycled materials is not fully understood. Knowing the wide variety of impurities that may be introduced in the recycling process, the objectives of this project are to determine the possible impurities, their role in structural stability, and their impacts (during synthesis and after synthesis) on the recovered NMC622 precursor and cathode materials.

Results

1. Characterization: Impurities

Initial effort has focused on the types and state of the various impurities that can be expected from a recycled cathode black mass (material recovered after shredding and sieving). For this study, black mass was obtained from Battery Resourcers (Worcester, MA). Materials are analyzed and baselined using standard analytical techniques including X-ray Diffraction (XRD), and Scanning Electron Microscopy (SEM). From XRD pattern, graphite, NMC cathode powder and Al_2O_3 were identified as crystalline components in the black mass. The morphology of the black mass is shown in the SEM image, showing separated NMC and graphite powder and agglomeration of the particles. Energy Dispersive X-Ray Diffraction (EDX) indicated that the black mass also contained measurable amounts of Al, Cu, carbon, and trace amounts of phosphorus and fluoride, which are components of the electrolyte salts and binders. The impurity and its concentration can be different depending on how the batteries are processed and the actual battery chemistry involved.

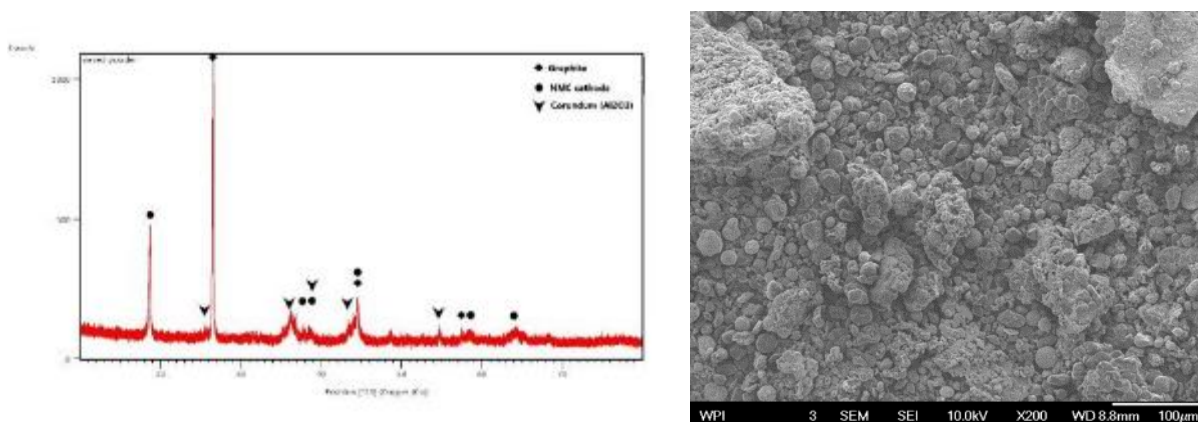


Figure 1. XRD and SEM of received black mass

2. Synthesis of NMC622 precursor and cathode materials without impurity

In order to establish baseline materials, we synthesized NMC622 precursors and cathode powders with virgin materials. Fig.2 shows the morphology of the precursor with the time. Initially, the particles are irregularly shaped and have low tap density. With the increased time, the particles become bigger, and more spherical, while the secondary particles are built of primary particles. Fig.3 shows the SEM and XRD with refinement of

synthesized NMC622 with 12hrs precursor. From SEM picture, the synthesized cathode powder is dense and has spherical shape. XRD analysis of the synthesized NMC622 matches the theoretical pattern. Refinement of the structure indicates that the Li/Ni anti-site cation mixing is 2.77%. This means that Ni^{2+} takes 2.77% of Li+ position in the crystal structure. Fig.4 shows the electrochemical properties of the synthesized NMC622, which shows reasonable rate performance and cycle life. The electrochemical performance is similar to the commercial baseline powders purchased by Argonne National Laboratory.

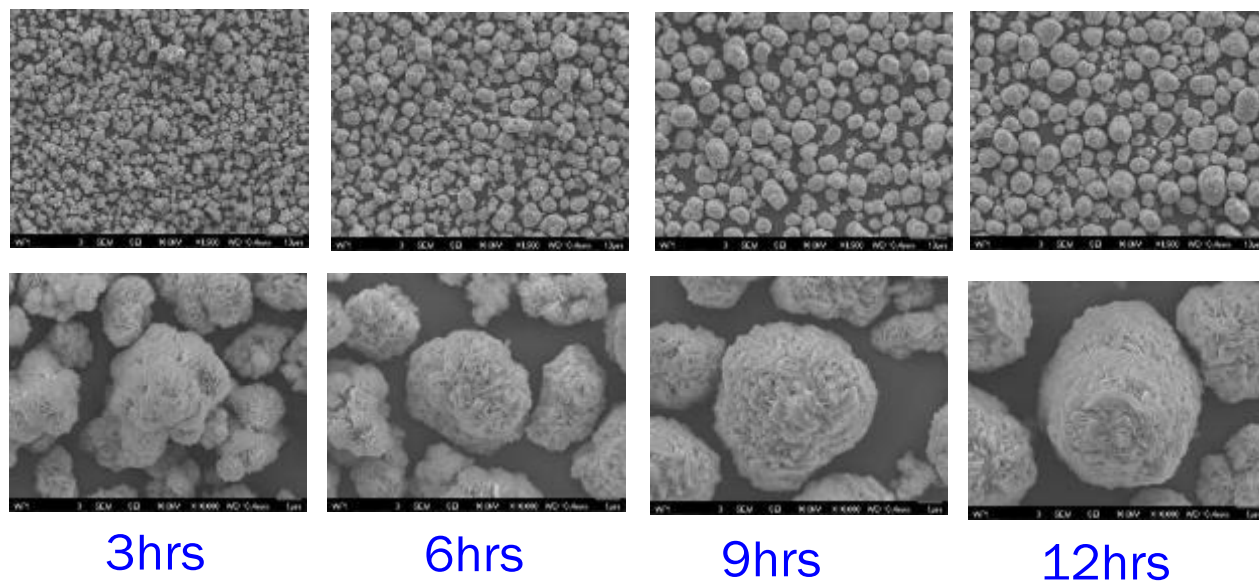


Figure 2. SEM of synthesized NMC622 precursor with time

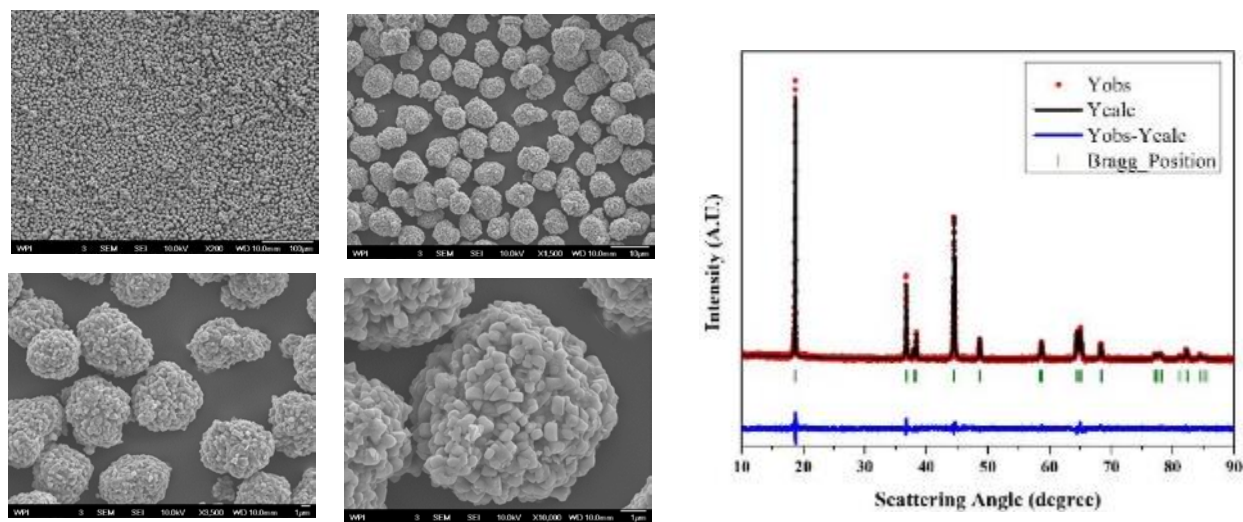


Figure 3. SEM and XRD of synthesized NMC622

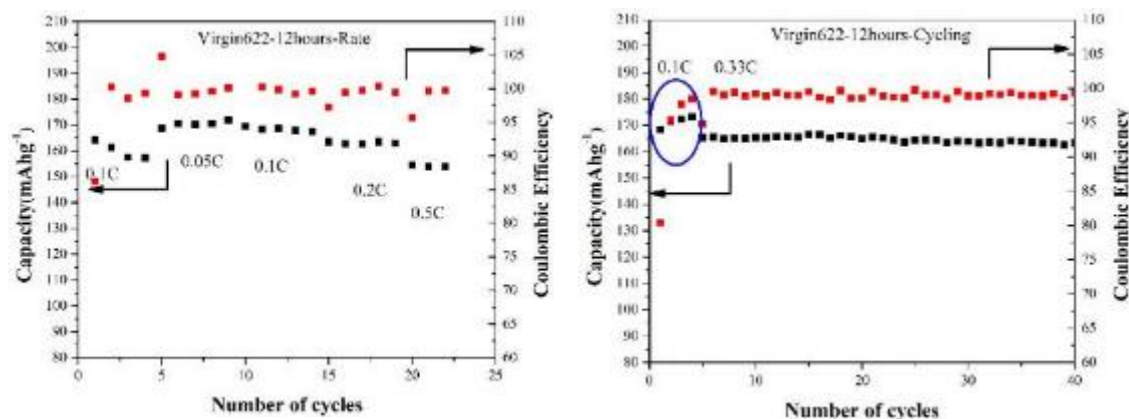


Figure 4. Electrochemical performance of synthesized NMC622

3. Synthesis of NMC622 precursor and cathode materials with Cu impurity

Cu or Cu ions have identified as the potential impurities during lithium ion battery recycling. Therefore, during the synthesis of NMC622 precursor, 5% of CuSO_4 was added into the metal sulfate precursor solution. Fig.5 shows the SEM of synthesized NMC622 precursor with Cu impurity at different times. Comparing to the SEM without impurity (Fig.2), the secondary particles in Fig.5 are bigger, less spherical and have lower tap density. Fig.6 shows the SEM and XRD of synthesized NMC622 with Cu impurity. Similar to its precursor, the cathode powder with impurity is less spherical. XRD pattern shows 2 weak impurity peaks and its refinement shows that the cation mixing is a bit higher (2.89% with impurity vs 2.77% without impurity).

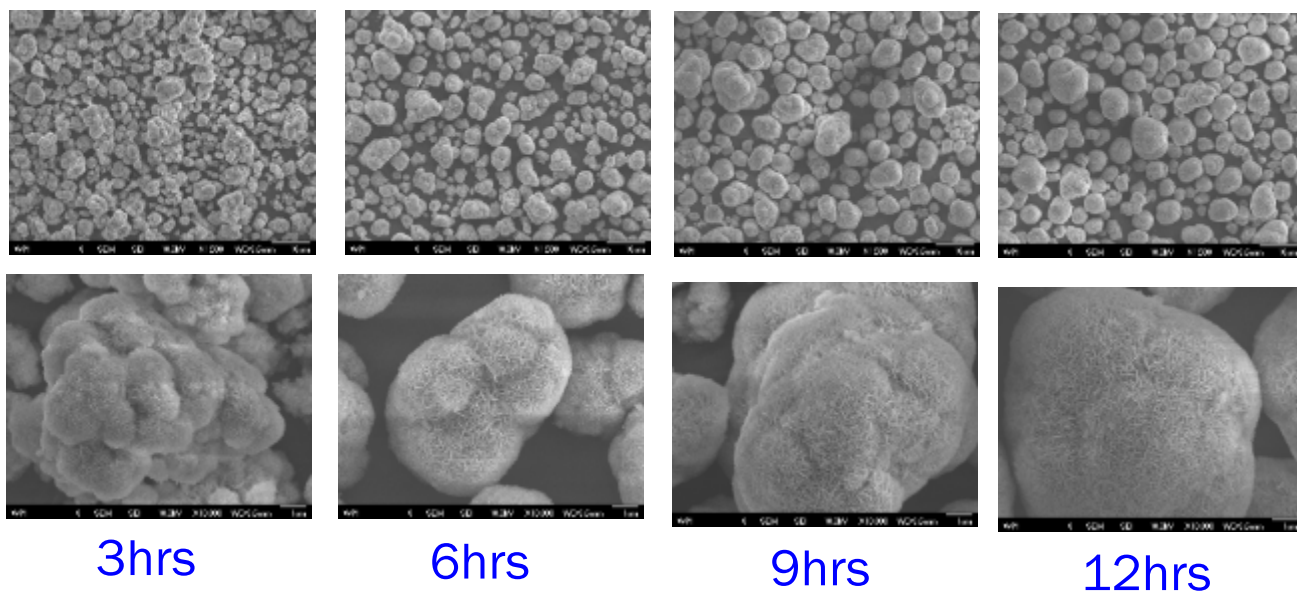


Figure 5. SEM of synthesized NMC622 precursor with impurity

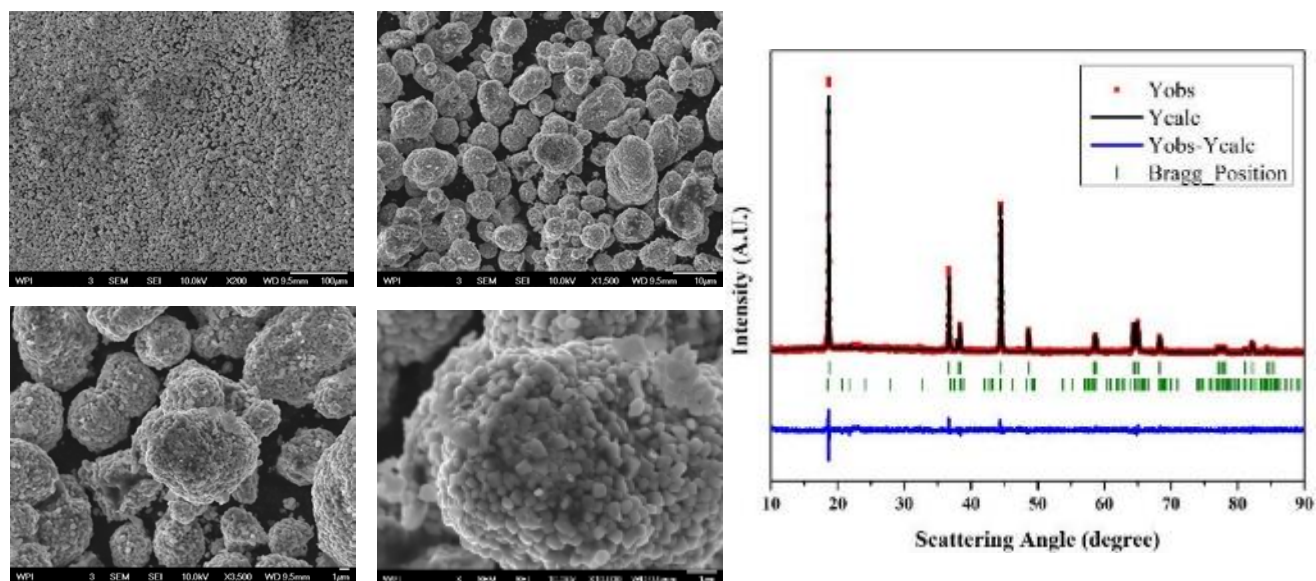


Figure 6. SEM and XRD of synthesized NMC622 with impurity

Conclusions

Analytical studies of the commercial black mass samples indicated that in addition to the NMC cathode and anode powders, the black mass was also found to contain Cu, Al (Al_2O_3), carbon powders, and trace amounts of salt or binder constituents. Differences in the impurity concentrations did depend on the underlying battery chemistry and the recycling process. Locally synthesized NMC622 has good morphology and tap density and electrochemical properties, when compared to program baselines. Introducing a Cu impurity was found to affect the morphology and structure of NMC622 precursor and cathode powder, which could affect its electrochemical properties, which will be reported in the next quarter.

Cathode Composition Change

Jack Vaughey, Tony Montoya (Argonne)

Background

The available batteries being supplied to recyclers is reflective of the popular battery chemistries from 5-10 years ago. This time lag between recycled materials and materials wanted by the marketplace may not be in sync over time as new chemistries and cell designs drive changes in supply and materials choices. Besides changes in the stream from material performance improvements and new chemistries, materials from non-transportation sectors may also play a role in adding anomalous materials to the waste stream, for instance LiCoO_2 from consumer electronics. In this effort we are designing and evaluating methods to change the metal ratios of recycled cathode materials to convert them to more current cathode formulations. This effort will initially focus on two raw materials, $\text{Li}(\text{NiMnCo})\text{O}_2$ (Toda 111) and LiCoO_2 and establish methods to utilize them as a feedstock material to produce other stoichiometries. An initial target will be NMC622.

Results

Initial work in this effort has focused on the stability of the cathode to defect concentration and treatment. As the process used will require higher temperatures than the re-lithiation process, the stability of the underlying lattice is an important variable. From a literature survey it was noted that one of the primary ways these layered structures eliminate defects is condensation to a structure such as spinel, where lithium vacancies are taken by Ni(II) diffusion from the transition metal layer above or below. This is manifested in a powder XRD pattern by the intensity ratio of certain peaks that reflect this site switch. As noted in Table 1, annealing the various samples at 500 °C was done to establish the stability and help define a simple diagnostic to check for this anti-site mixing. As anticipated the post annealed sample with no significant lithium site defects showed stability in the ratio and maintained their primary lattice positions, while the delithiated sample (Toda 111, MERF) showed a collapse of the ratio, indicative of more significant site mixing and movement of the Ni(II) to the lithium sites.

Table-1: X-ray diffraction peak intensity ratios for treated NMC111 materials.

Annealing performed at 500 °C under an air atmosphere.

	Ratio of I_{003}/I_{104}	Ratio of I_{003}/I_{104} (Post anneal)
Pristine NMC 111	1.29	1.27
Delithiated NMC 111	1.26	1.04
NMC Relithiated (Li_2CO_3)	1.33	1.35

Future work will utilize LiCoO_2 as a stable baseline material as Co(III) is electronically inhibited from diffusing into the lithium layer under normal circumstances (although LiCo_2O_4 spinel has been reported from delithiated Li_xCoO_2 in a long term annealing study), Alternative cathode materials will be created and evaluated. Initial methods will use methods analogous to making gradient cathodes as a starting methods. In addition, methods to convert NMC 111 to more nickel rich materials will be investigated in association with CAMP, MERF, and EverBatt teams.

Conclusions

Initial work has highlighted the need to minimize defects in the host lattices and we have confirmed the utility of using selected peak ratios in these layered NMC samples as a quick diagnostic for assessing the anti-site mixing of the constituents.

Recovery of Other Materials

Lithium Ion batteries are made up of a number of valuable materials. In the first area of this program, cathode recovery was the focus of the work. Critical materials and high processing cost goes into making cathode materials, making them important to recover as close to a reusable form as possible. There are other materials that are present in lithium ion batteries that are just as critical and are costly to produce.

In this area of the program, Other Materials Recovery, the projects are focusing on recovering those materials. Graphite and lithium are two other critical materials that are present in cells. These materials are defined as critical because they are in limited quantity around the world or the location that they are produced in are not stable. By recovering these materials we will be securing a source of these materials, therefore reducing the foreign dependence on these materials and increasing our national security.

Again just like the cathode, LiPF₆ (one of the electrolyte salts), has a high production cost because of the fluorine chemistry and waste products. By recovering LiPF₆, this material can be reused in batteries, thus reducing the cost and environmental impact that this material has.

By recovering additional materials, the recycling process maximizes the reuse of lithium ion cell components and therefore increasing the revenue in the recycling process and driving the overall process to profitability.

This section covers projects on, Hydrothermal Recovery Process for the Black Mass, Anode/ Cathode Separation and Purification and Electrolyte Components Removal and Recovery. Each of these projects address an additional material stream that can be recovered and sold to drive the recycling process towards profitability.

Electrolyte Components Removal and Recovery

Albert L. Lipson, Seth Reed (Argonne)

Background

Electrolyte during the recycling process needs to be removed from the materials to allow for further processing to recover cathode and anode materials. Electrolyte materials are sensitive and undergo decomposition when exposed to moisture for prolonged time. Electrolyte solvents are also volatile, toxic and flammable. Due to the instability and for a safety reason, removal of electrolyte materials should be the first step in the chain of recovery and recycling battery materials. This can be done in several ways including supercritical CO₂ extraction, thermal drying-removal of solvents, water washing and solvent extraction. Of these only supercritical CO₂ with added co-solvent or solvent extraction can recover the LiPF₆, which is the most valuable component of the electrolyte. In either of these processes it is critical to know the impurities, the different electrolyte compositions and how these may impact electrochemistry and the recycling process. Alternatively, water washing can generate LiF that could potentially be recovered, and sold to be use as a feedstock for manufacturing LiPF₆. In addition, water washing may be able to remove SEI components from the anode thereby recovering additional Li.

Results

Electrodes that had been harvested from a cycled OEM battery were utilized as the starting material for this project. These electrodes were then soaked in different solvents to extract the electrolyte, and then the electrodes were removed. The resulting mixtures were analyzed by nuclear magnetic resonance (NMR) and gas chromatography with mass spectrometry (GC-MS) to determine impurities and the electrolyte composition. The ¹H and ¹⁹F NMR are shown in figure 1. Based on these results and scanning electron microscopy energy dispersive X-ray analysis (SEM-EDX) the electrolyte appears to be a mixture of LiPF₆ salt, ethylene carbonate (EC), propylene carbonate (PC), diethyl carbonate (DEC), ethyl methyl carbonate (EMC), and a silicon containing additive. It is also apparent in the ¹H NMR and ¹⁹F NMR that there is a decomposition product of EC and some hydrolysis of LiPF₆ to LiPO₂F₂. There are also many small peaks that may indicate additional impurities, such as PVDF and other additives. This very complex electrolyte indicates the difficulty of trying to recycle electrolytes especially when there is a mixture of electrolyte compositions from different manufacturers.

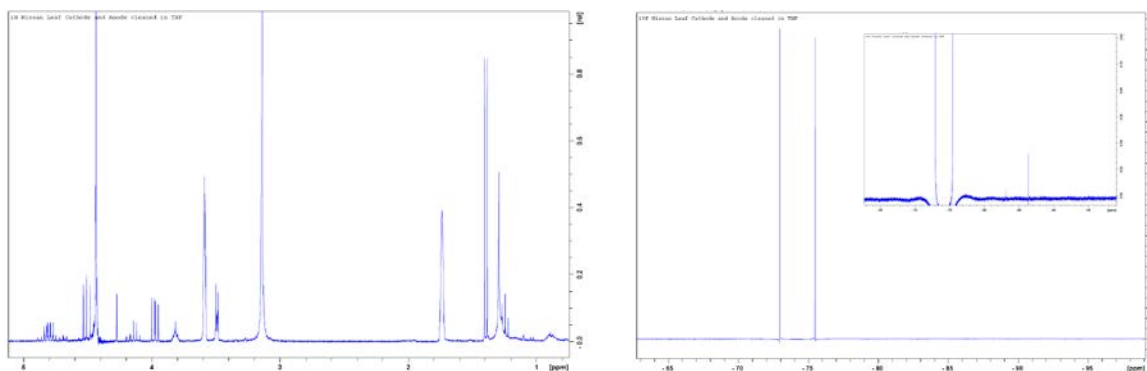


Figure 1. ¹H (left) and ¹⁹F (right) NMR of cycled Nissan Leaf electrolyte dissolved in deuterated THF. Inset shows a zoomed in region to be able to see the LiPO₂F₂ peaks.

Since the impurity analysis showed very similar impurity profiles between the four solvents (acetonitrile (ACN), dimethyl formamide (DMF), tetrahydrofuran (THF), and diethyl carbonate (DEC)), we

evaporated off the solvents and looked at the crystals left behind. The X-ray diffraction (XRD) pattern didn't match either EC or LiPF₆ likely indicating that the material was a complex formed between the solvents and LiPF₆. To analyze these samples further we decided to dissolve them in deuterated THF and perform NMR spectroscopy. The results are similar to the as extracted material in ¹H NMR, except for peaks that appear to correspond to PVDF at 3.8 ppm and a possible additive at 3.5 ppm that are greatly diminished in the recrystallized sample. However, in the ¹⁹F NMR we found that ACN and THF had significant hydrolysis of the LiPF₆, whereas DMF and DEC looked just as pure as before recrystallization. From these results, and the finding that it had the highest yield, DEC was chosen as the solvent for extracting electrolyte. We then tried to run half cell Li batteries using this extract as the electrolyte, but the cells failed after the first charge. This is likely due to the additives reducing on Li metal and blocking the electrode. Full cells will be tried to resolve this issue.

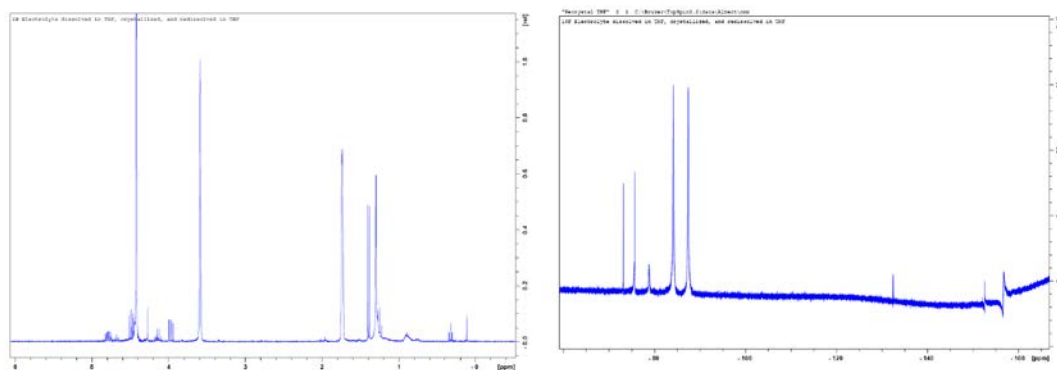


Figure 2. ¹H (left) and ¹⁹F (right) NMR of cycled Nissan Leaf electrolyte dissolved in deuterated THF, recrystallized and redissolved in deuterated THF.

In addition to the solvent extraction methodologies, we have also looked into the possibility to dissolve solid electrolyte interphase (SEI) products on the anode to enhance Li recovery from the batteries to be recycled. After a solvent extraction to remove the majority of the electrolyte, the anode was soaked in either hydrochloric acid or deuterated water. The extracted liquid was measured using ICP to determine the Li content. It was found that 1.4 wt.% Li was extracted from the anode in hydrochloric acid, and 2.2 wt.% Li was extracted in deuterated water. This corresponds to 10% and 16% of the cathode's Li content, which are close to the expected Li loss to the SEI. Deuterated water was used to be able to look at the ⁷Li spectra, and it shows a single sharp peak at 0.11 ppm, which indicates a single Li environment. This extracted Li could be used to make LiOH, Li metal or other products via known processes.

Conclusions

It is possible to recover reasonably pure electrolyte through the use of solvent extraction using DEC as the solvent. The effect of the remaining impurities on the electrochemistry in a recycled cell is still unclear, but it may be necessary to implement additional purification steps to reuse this electrolyte. There are a number of options of how to finalize the processing of the material with possible products being the recrystallized material, electrolyte that has been concentrated to match standard concentrations, or dilute electrolyte that can either be reformulated at the recycler or sold directly. These processes and possible end products are being cost modeled to determine their profitability. In addition to the solvent extraction efforts, the potential to have a water-based process, which could still yield LiF as a product, is being explored.

Milestones and Deliverables

Task 1 (M1-3) Acquire appropriate black mass feedstocks (Completed)

Electrodes from an OEM's batteries were acquired and were used as a model material.

Task 2.1 (M3-6) Utilize various solvents to extract electrolyte from the black mass (Completed)

Several different solvents have been investigated and efficiency to extract electrolyte materials evaluated.

Task 2.2 (M4-10) Determine yields and impurities of extracts from tasks 1-3 utilizing NMR, FTIR, XRD, and GC-MS as appropriate (In Progress)

Most of the experiments have been completed. Purity of the removed and recovered electrolyte components have been investigated using various analytical techniques. Quantitative studies are in progress.

Hydrothermal Recovery Process for Black Mass

Ilias Belharouak, Nitin Muralidharan, Jianlin Li, Huimin Luo, Zhijia Du, Sheng Dai (ORNL)

Background

Li-ion batteries have been a key driving factor in the technological revolution of portable electronic devices. In recent years, the advent of electric vehicle technology has once again galvanized the alkali metal ion battery industry and has ushered in a period of rapid advancement which is expected to only substantially increase in the near future. This boom, however, leaves a conundrum as well as an opportunity which warrants a closer investigation. This scenario is due to the rising amount of end of life, defective and failed lithium ion battery packs and cells which must be properly disposed of or recycled to avoid significant environmental issues. Recently, recycling of such Li-ion cells has garnered great interest in both industrial and academic sectors owing to the rapid rise in cost of raw materials, especially cobalt and scarcity of certain raw materials for manufacturing lithium ion systems. Moreover, if recovery and reuse of valuable materials such as cobalt, nickel, copper and aluminum are possible, then that also provides an economic incentive for industries to pursue the Li-ion battery technology unhindered. In this regard, this work deals with the hydrothermal recovery process for the 'black mass', a term defining the aggregated mixture of active material (both anode and cathode), conductive additive and binder from end of life, defective or failed lithium ion batteries and packs. The preliminary findings reported here enable feasible routes which can be further optimized for the recovery of 'black mass' using hydrothermal method thereby providing a broad framework for recycling of lithium ion battery systems.

Results

Recycling approaches for lithium ion battery systems must consider the chemistries of distinct components of the battery which behave differently to the different recycling methodologies investigated. In commercial Li ion systems, binders are an integral part of the electrode architecture which holds the carbon containing active material (anode or cathode) coating with itself and with the metallic current collectors (Cu or Al). If electrode coatings must be separated from the metallic current collectors, dissolving the binder provides a promising approach to investigate first.^[1] Our initial approaches controllably investigated the solubility of a commercial PVDF binder (SOLEF 5130) in different mixtures with varying NMP (known solvent for PVDF) and water. Figure 1 shows the dissolution studies of PVDF in NMP/H₂O mixtures where it can be inferred that in order to completely dissolve PVDF without any partial or severe phase separation, NMP/H₂O mixtures with high NMP content (~90%) are required.

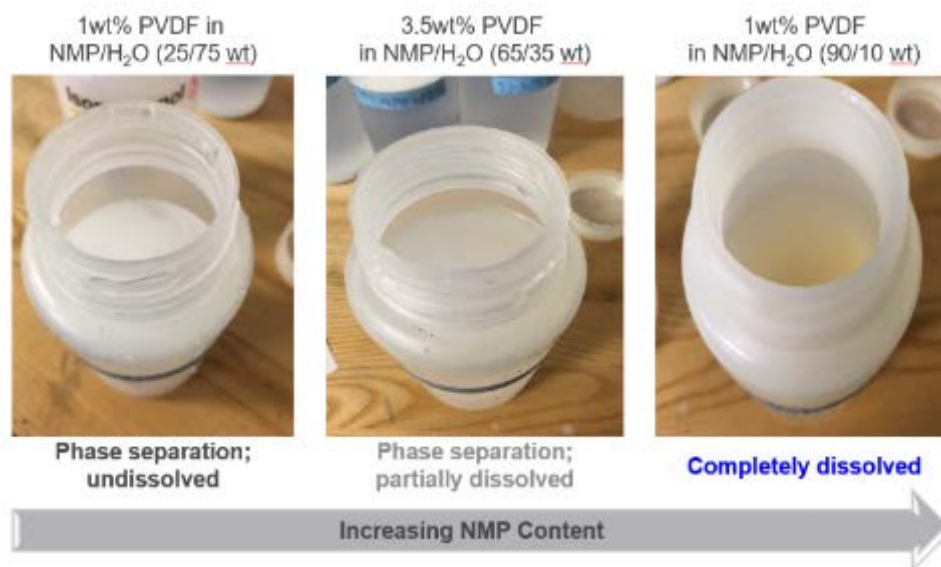


Figure 1. Dissolution studies of PVDF (5130, SOLEF) in NMP/H₂O mixtures

Based on the findings of our binder dissolution studies, electrode coatings were subjected to a hydrothermal treatment at 170 °C for 24 hours in various NMP/H₂O mixtures to dissolve the binder and separate the current collector and the black mass. Figure 2 show the scanning electron micrographs of the NMP/ H₂O hydrothermally treated NMC 622 electrode coating. It can be observed that in the presence of water, the aluminum current collector undergoes corrosion owing to the possible increase in basicity of the reaction mixture as a result of lithium leaching from the active materials. This causes the aluminum to corrode and deposit on the cathode particles. SEM micrographs for the hydrothermal treatment in 100% NMP show complete separation of the active material (NMC 622) and the aluminum current collector without any significant corrosion. However, owing to the high toxicity and environmental costs associated with NMP handling and usage, alternative solutions must be explored and investigated.

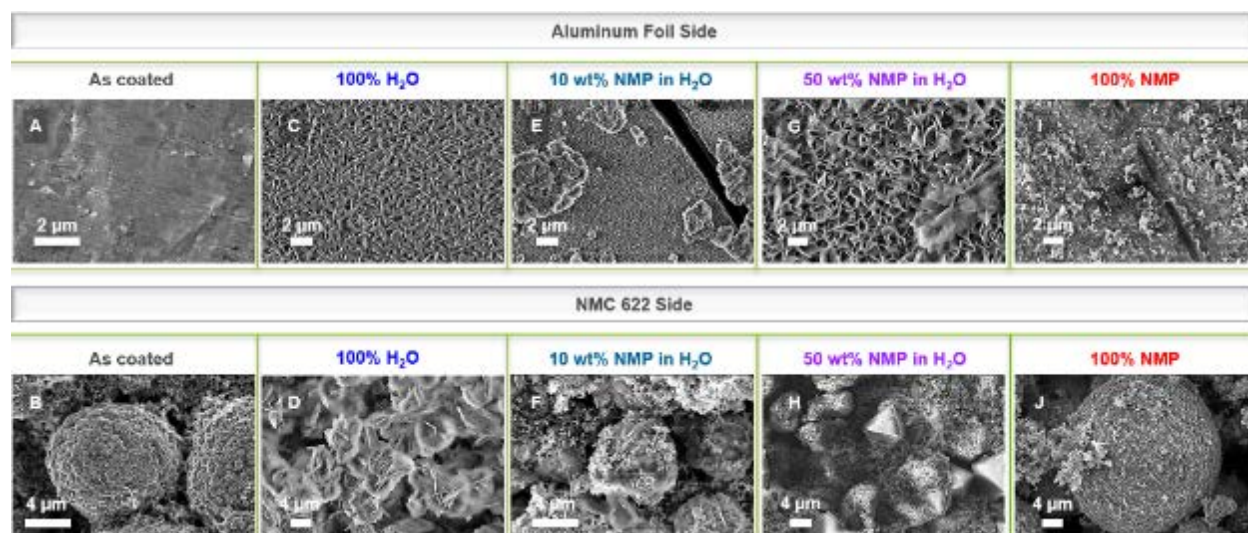


Figure 2. SEM micrographs of NMC 622 Coated on Aluminum Foils after hydrothermal treatment in various NMP/H₂O mixtures: A,C,E,G, I show the aluminum foil side and B,D,F,H, J show the NMC 622 cathode side

Even though, using 100% H₂O is not a viable option to separate the cathode active material from the aluminum current collector, the same approach for the anode side enables complete separation of the current collector from the active material. Figure 3 shows the optical and SEM micrographs of graphite coated on copper foils after hydrothermal treatment in H₂O. It can be observed that separation of black mass was easily achieved through this approach for the anode side.

As an alternative approach, leveraging the known dissolution behavior of aluminum in basic solutions^[2], hydrothermal treatment of NMC 622 coated aluminum foils were performed in various solutions with different basicity. Lithium hydroxide (LiOH) and water mixtures of varying concentrations with varying basicity were used in this approach. Figure 4 shows the SEM micrographs of the aluminum and NMC 622 side after hydrothermal treatment in varying LiOH/H₂O mixtures. It can be inferred from the SEM micrographs that although complete dissolution of aluminum current collector is achieved with treatment of 0.6M LiOH in H₂O, the dissolved aluminum gets precipitated in its compound forms onto the NMC 622 particles thus causing challenges in recovery of the active materials.

Our preliminary work so far highlights the challenges and feasible approaches towards recovery of black mass using hydrothermal techniques for Li-ion battery recycling. Despite the challenges, further optimizations of process parameters such as time, temperature, pH, mechanical stirring rate and pressure can enable effective recovery of black mass using these approaches. Further optimizations are currently being pursued as a result of the findings from our investigations so far.

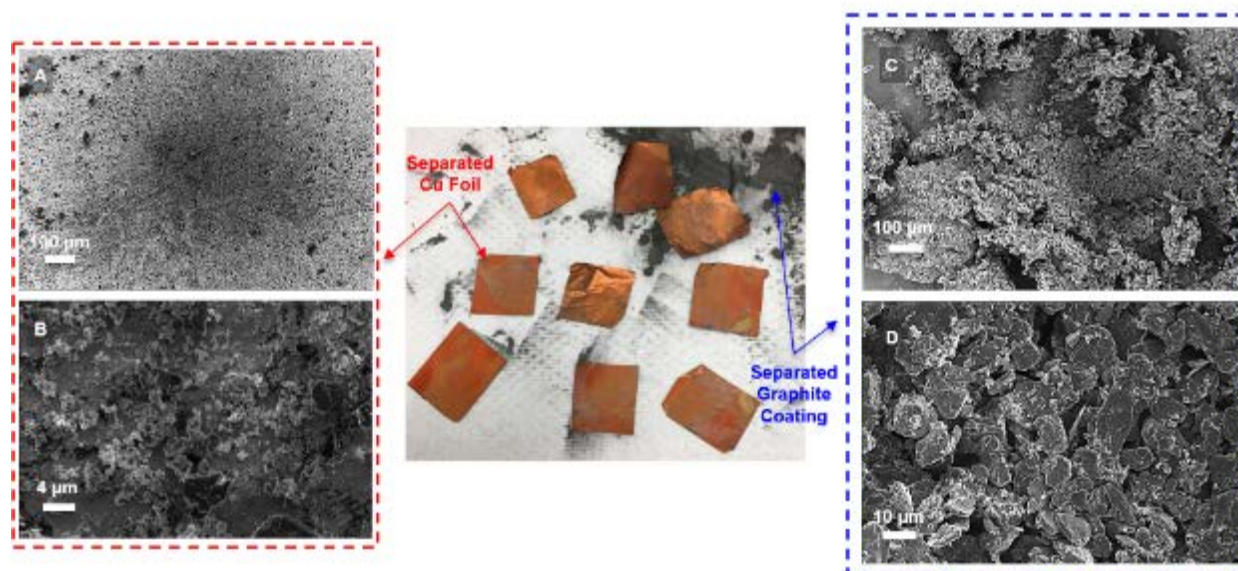


Figure 3. Optical and SEM micrographs of graphite coated on copper foils after hydrothermal treatment in H_2O : A, B show the copper foil side and C, D show the separated graphite anode side

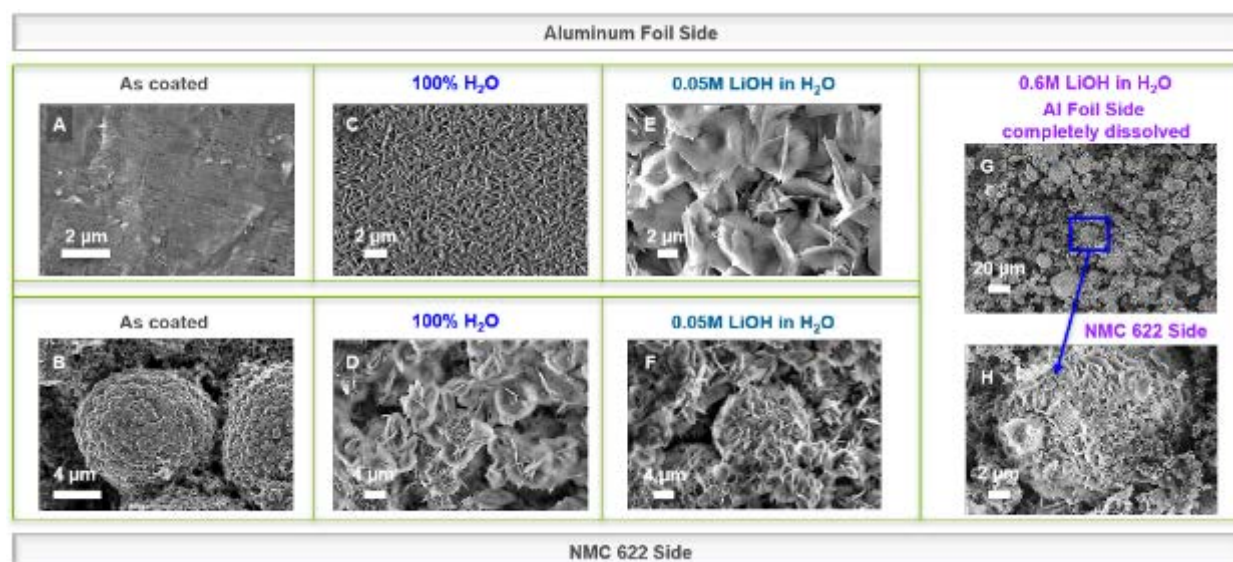


Figure 4. SEM micrographs of NMC 622 Coated on Aluminum Foils after hydrothermal treatment in solutions containing different concentrations of LiOH: A, C, E, G show the aluminum foil side and B, D, F, H show the NMC 622 cathode side

Conclusions

In summary, from our investigations we infer that separation and recovery of anode (graphite coating and copper) was easily achieved through the hydrothermal treatment in DI water at 170 °C for 24 hrs. However, on the cathode side, separation of cathode coatings using the same approach poses challenges as aluminum undergoes corrosion with increase in pH owing to the presence of mild LiOH when treated with DI water. Two approaches were therefore investigated; (i) Using mixtures of NMP and water to dissolve the PVDF binder in these coatings

thereby easily separating the coating and current collector and (ii) Dissolving Al completely through the hydrothermal treatment in basic environment using increased LiOH concentrations. Using Al dissolution approach the recovery of aluminum is challenging and thus requires optimization. On the other hand, the approach using NMP/water mixtures in various ratios provides a promising direction for further investigations through the optimization of hydrothermal treatment parameters such as Temperature, Time, stirring conditions and pH controls.

Milestones and Deliverables

Task 1 (M1-2): The hydrothermal setup has been installed and the instrument to shred electrodes ready.

Task 2 (M3-6): Cut electrodes into various sizes and evaluate feasibility of separating electrodes from the metallic foils via hydrothermal treatment using various solvents formulation and process parameters.

References

- [1] Aparicio. S. et al., J. Phys. Chem. B 2008, 112, 11361-11373.
- [2] OPERA-PU-IBR511B: Corrosion behavior of spent research reactor fuel under OPERA repository conditions (2016)

Anode/Cathode Separation and Purification

Erik Dahl (Argonne)

Background

Most recycling efforts focus on recovering the cathode materials and metals, which neglects the potential value from recovering anode material. The focus of this project is to separate and recover usable anode materials from black mass. The cost contribution of anode powder in a typical cell is 11%. The cost effective recovery of anode powders from end-of-life batteries for reuse in new batteries will add a new revenue stream making battery recycling more cost effective overall.

Many methods of separation are planned. These include screening, air classification, and magnetic separation. Binary mixtures of NMC111, LMO, NCA, LFP, LCO and graphite have been prepared and will be used to test different separation techniques. Initial tests will be conducted with 50/50 mixtures. As work progresses the mixtures will become more complex and will include all of the relevant cathode materials mixed with graphite. Additionally actual black mass from shredded end of life batteries has been acquired. This material is currently being characterized and will eventually be used to test separation and purification techniques developed using model mixtures.

Currently two air classification units are being prepared for use. One is an aspirator classifier which will separate the fine powders from other detritus present from shredding the shell. The second unit is a turbo classifier which is capable of separating micron sized particles. This unit will be used to remove fine contaminants that remain after the first classification stage. It is possible that this unit may also separate some amount of cathode powder during this process.

Results

Preliminary tests of magnetic separation of graphite and LMO were conducted using a series of permanent magnets of increasing strength. Mixtures of 50% of pristine graphite and 50% LMO were allowed to slide under the force of gravity over a magnet covered by weighing paper. The material retained by the magnet was labeled and saved for characterization. Three experimental conditions were replicated three times and the results are shown in table 1.

Table-1: Magnetic Separation of graphite from LMO cathode powder

Residual Flux Density [G]	Percentage of LMO separated from Graphite			
	Run 1	Run 2	Run 3	Average
7000	73.3%	72.4%	71.0%	72.2%
8300	83.6%	84.0%	82.0%	83.2%
9600	96.7%	93.0%	97.0%	95.6%
10300	95.2%	99.1%	97.7%	97.3%
12300	98.5%	98.0%	99.1%	98.5%
13050	99.1%	99.3%	99.1%	99.1%

13500	99.9%	99.9%	99.9%	99.9%
14000	99.9%	99.9%	99.9%	99.9%
14800	99.9%	99.9%	99.9%	99.9%

Conclusions

Magnetic separation of graphite from LMO is quite effective and does not require especially powerful magnets to remove the majority of LMO from graphite. More experiments are currently underway to determine separation efficiency of mixtures of anode with various cathode chemistries. A search for a suitable commercial magnetic roll separator that would allow more rigorous process development is underway.

Milestones and Deliverables

Task 1 (M1-2) Acquiring various commercial cathode chemistries and mix with anode powder to produce model black mass - Complete

Task 2 (M1-2) Determination and demonstration of feasible separation technologies - Complete

Task 3 (M4-10) Testing and evaluation of air classification magnetic, and flotation techniques – In progress

Design for Recycle

Millions of batteries are approaching their end of life and need to be recycled. While many efforts have been focused on recycling the elements and/or compounds from spent cells through various techniques, this focus area aims to create cell designs that will enable rejuvenation of a spent cell, and/or improve the ease of recycling at the end of life. The ability to regenerate a cell with an electrolyte flush/rejuvenation has the potential to extend the life of a lithium-ion battery far beyond its typical 10-year life. This will reduce the amount of packs requiring recycling and/or make for easier target material extraction.

Design for Recycle – Cell Design

Jianlin Li¹, Anand Parejiya¹, Sergiy Kalnaus¹, Andrew Jansen² (¹ORNL and ²Argonne)

Background

Millions of batteries are approaching their end of life soon and need to be recycled. While many efforts have been focused on recycling the elements and/or compounds from spent cells through various techniques, this project aims to create cell designs that will enable rejuvenation of a spent cell, and/or improve the ease of recycling at the end of life. The ability to regenerate a cell with an electrolyte flush/rejuvenation has the potential to extend the life of lithium-ion battery far beyond its 10-year life. This will reduce the amount of packs requiring recycling and/or make for easier target material extraction. The cell-making capabilities in Cell Analysis, Modeling, and Prototyping (CAMP) Facility and Battery Manufacturing Facility (BMF) collaborate to design, model, prototype, and test novel cell designs that can be rejuvenated. BatPaC will be utilized to model gravimetric and volumetric energy density of the new designs to determine their viability. Selected cell designs that meet established criteria will be tested in prototype cells.

Results

Pressure-Flow Study in Cylindrical Cell Design

In this study, the 18650 cell format will be used to test the relationship between applied flow of a solvent longitudinally through an interior cell winding. A simplified approach was adopted where the solvent ports are on opposite ends of the cell as shown in the left side of Figure 1. A test fixture was designed in the 1st Quarter and built in the 2nd Quarter (Figure 1, right). Preliminary cell windings were made using available electrodes while the final double-sided baseline electrodes were being fabricated (see below). A peristaltic pump and tubing were selected, ordered and received in the 2nd Quarter. This setup is now being assembled and will be tested with propylene carbonate as the model solvent. Methods are being developed to seal the outer diameter of the cell assembly to the test fixture and to plug the central hole in the cell assembly to prevent solvent flow bypassing the electrode/separator pores.

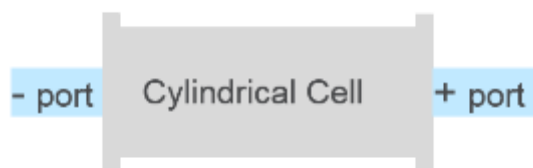


Figure 1. Baseline port design for cylindrical cell with solvent flow capability (left); and test fixture and preliminary cell assembly for testing solvent pressure-flow relationship.

Double-sided Baseline Electrodes

The pressure-flow relationship must be determined in electrodes and separators that are likely to be produced in the near future. It is anticipated that these electrodes will use NMC-based cathode powders and graphite anode powders with capacity loadings near 3 mAh/cm² on each side of the electrode. In the 2nd Quarter, capacity-matched double-sided graphite anode (SLC1520P, Superior Graphite) and NMC cathode (NMC622, Targray) were fabricated. The details of these electrodes are provided in Figure 2. These electrodes will be

used in 18650 cell windings with Celgard 2320 separator, and tested in the pressure-flow fixture recently machined.

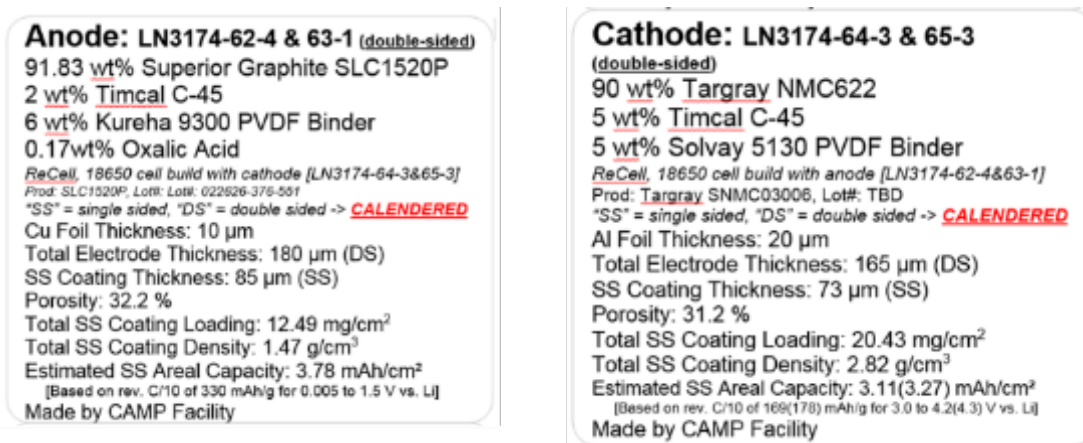


Figure 2. Baseline double-sided electrodes to be used in the solvent pressure-flow study.

Pouch Cell Design for Rejuvenation

Besides the 18650 cell format, pouch cell format was also investigated. Figure 1 shows a schematic (1st Quarter) and actual design (2nd Quarter) on pouch cells which allows us to flow a solvent through the cells. Two ports (5 mm diameter) were applied to the sides since there are more space to work with. The ports can be applied to the top and bottom as well. Challenges during the cell fabrication with new design was mainly on sealing the cell with the ports. Several versions were investigated, and two switches were selected eventually.



Figure 3. Baseline port design for pouch cell with solvent flow capability (left); and preliminary cell assembly for testing solvent pressure-flow relationship.

Pressure-Flow Study in Pouch Cell Design

ORNL provided NMC622 powder to Argonne for electrode fabrication and received Celgard 2320 separator from Argonne for this project. BMF also fabricated NMC622 cathode with same specifications as listed in Figure 2. A pouch cell was assembled with ad-coated electrode to monitor pressure during solvent injection. A syringe pump was ordered (2nd Quarter) and a test fixture was built as shown in Figure 4. A load cell was used to monitor cell pressure.



Figure 4. Test fixture for testing solvent pressure-flow relationship.

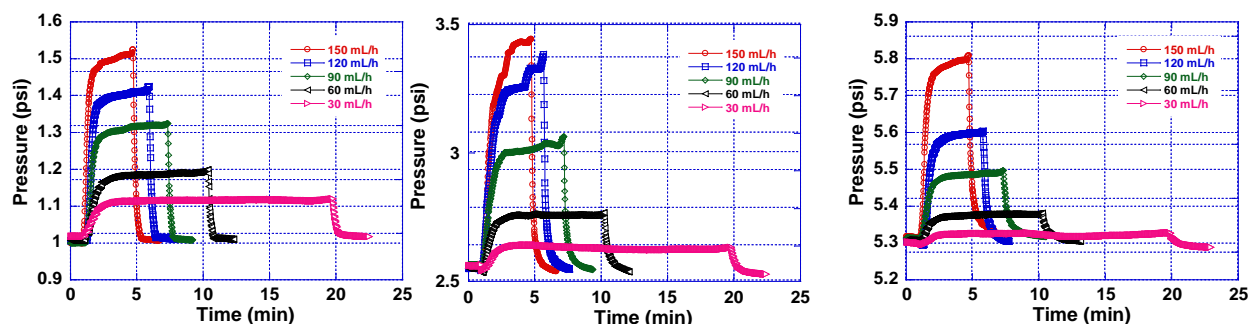


Figure 5. Pressure-flow relationship with various external compression.

Figure 5 shows the pressure-flow relationship with various external compression. For this initial study, isopropyl alcohol (IPA) was used as the solvent to flush through an as-assembled pouch cell. Three external compressions (1, 2.5 and 5.3 psi) were chosen which are relevant to the practical application. After applying the external compression, the cell was rest until the pressure stabilized before starting experiment. Five flow rates (30, 60, 90, 120, and 150 mL/h) were used. The pressure increased with increasing flow rates. After the solvent injection was completed, the cell pressure returned to the external cell compression. The pressure increased more when increasing the external compression from 1 to 2.5 psi and reduces when further increasing from 2.5 to 5.3 psi. This may indicate some by-pass of liquid between the jelly roll and pouch material.

Conclusions

In this project period, we have designed and fabricated texture to characterize pressure-flow relationship for both cylindrical and prismatic cell formats. Electrodes have been coated for this project. Initial pressure test has been carried out. Reasonable pressure increase was observed which indicated that solvent can be flushed through cells.

Milestones and Deliverables

Tasks/Milestones:

- Task 1 (M1-6):** Design cylindrical (AL) and prismatic cells (ORNL) with ports with enough detail to estimate impact on cell energy density.
- Task 2 (M3-6):** Fabricate test fixture to measure flow rate as a function of pressure

Modeling and Analysis

The modeling and analysis focus area includes four subareas: diagnostics on aged materials, microcalorimetry on recycled materials, cost and environmental impacts modeling, and battery supply chain modeling. The first two subareas characterize battery materials via electron backscattering diffraction (EBSD) and with a microcalorimeter, respectively, to evaluate the performance of battery materials under various conditions, while the last two subareas evaluate the economic and environmental impacts, as well as the material flows, pertaining to the battery supply chain. The four subareas will work together to identify the optimal recycling processes for batteries, and will serve to inform and direct the R&D efforts under the ReCell Center.

Major efforts made under the modeling and analysis focus area during the first and second quarters of fiscal year (FY) 2019 are summarized in Table 1. Detailed information about individual project progress and latest results are provided in the subarea reports below.

Table-1: Modeling and Analysis Focus Area Major Efforts in Q1 and Q2 FY2019

Subarea	Major Efforts
Diagnostics on Aged Materials	Set up a process to resolve grain size and orientation in various cathode materials using EBSD; Completed methodology report
Microcalorimetry on Recycled Materials	Set up the microcalorimeter
Cost and Environmental Impacts Modeling	Updated data and refined cost modeling in EverBatt; Drafted model documentation
Battery Supply Chain Modeling	Analyzed the supply and demand relationships for cobalt and lithium; Published a draft user interface of the LIBRA model

Diagnostics of Aged Materials

Shriram Santhanagopalan, Kae Fink, Helio Moutinho, Andrew Norman (NREL)

Background

There are trade-offs between recycling a vehicle battery at the end-of-life criteria set forth for the vehicle versus extending the usable range of the battery. Similar trade-offs exist in keeping recycling streams separate, versus co-mingling materials from cells with different histories.

This task evaluates the extent of material degradation in cell components under different end-of-life conditions and aims to provide technical rationale and diagnostic criteria to determine the suitability of specific recycling methods. In particular, characterizing aged electrode material as a function of operating voltages and C-rates will:

- 1) Identify chemical signatures corresponding to efficiency losses from calorimetry measurements;
- 2) Inform electrochemical relithiation conditions; and
- 3) Match the extent and type of degradation to target recycling methods, based on load profiles, cycling windows, and cost metrics

Results

Methods have been developed to obtain grain orientation from cathode samples via EBSD. Sample preparation for EBSD analysis includes immobilization of cathode samples, polishing and ion milling of a cross-section (Figure 1 (a)-(b)). Initial STEM studies are also underway, with samples cross-sectioned via FIB lift-out and subsequently ion milled (Figure 1 (c)-(d)).

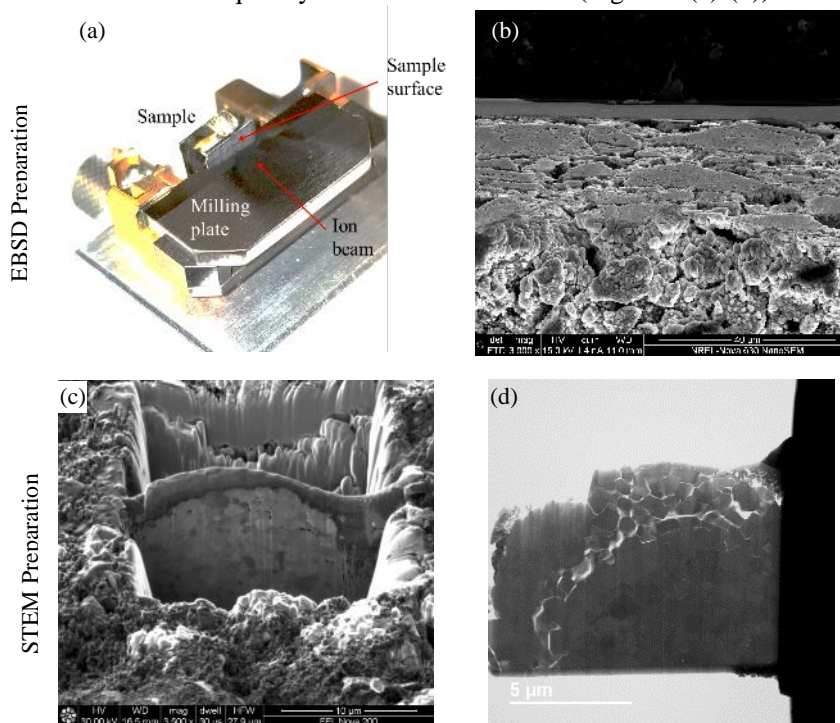


Figure 1. Sample preparation methods for EBSD and STEM analyses: (a) Ion milling protocol (EBSD); (b) SEM image of polished and ion-milled NMC sample (EBSD); (c) SEM image of a trench in an NMC sample during FIB liftout (STEM); (d) Bright-field STEM image of a FIB cross-section (mounted on post) (STEM). Figure Credits: Helio Moutinho, Andrew Norman, NREL.

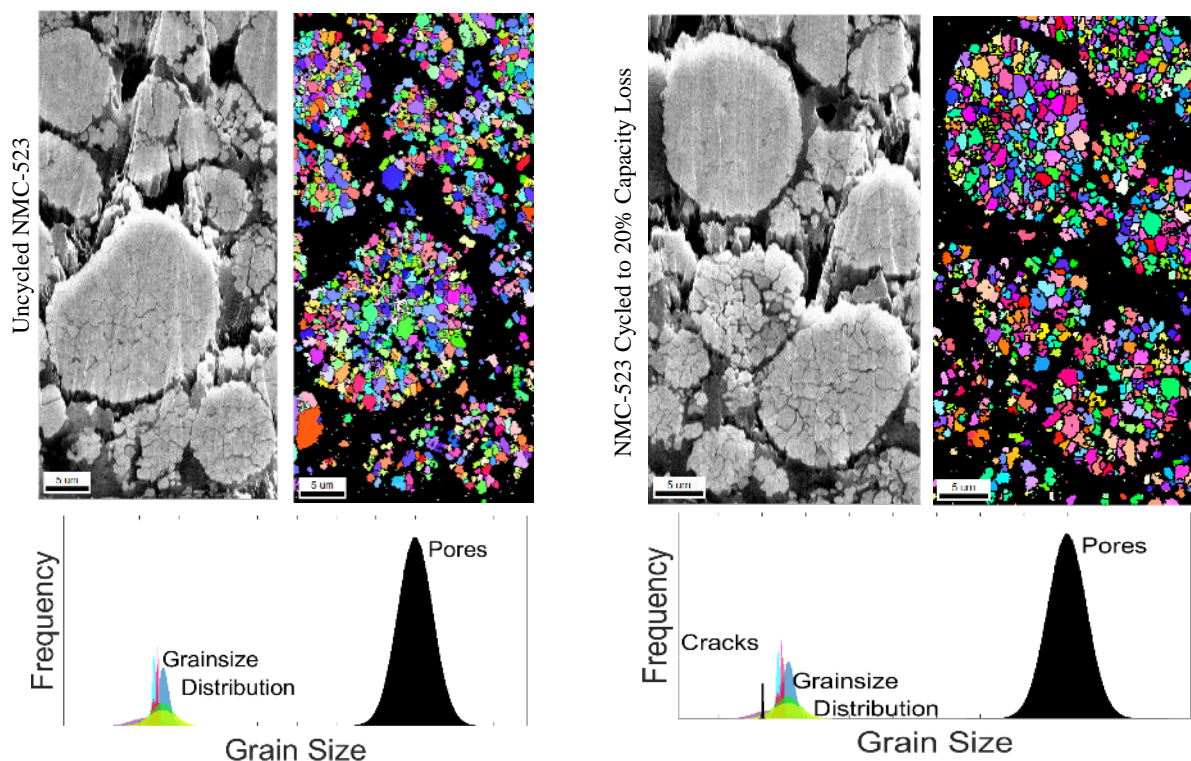


Figure 2. EBSD patterns from SEM cross-sections and corresponding grain size distribution for NMC523 samples: uncycled (left) and cycled to 20% capacity loss (right). Each color on the EBSD spectrum represents a different grain orientation of the cathode primary particles. Figure Credits: Helio Moutinho, Shriram Santhanagopalan, NREL.

EBSD data has been collected for off-the-shelf $\text{LiNi}_{0.5}\text{Mn}_{0.2}\text{Co}_{0.3}\text{O}_2$ (NMC523) samples, both dry (uncycled) and cycled to 20% capacity loss (Figure 2). EBSD patterns observed after 20% loss of capacity indicate no significant changes to particle size, grain orientation, etc. except for the appearance of some hairline cracks. Some grain orientations show attrition, but no statistically significant patterns have emerged yet. Analysis of preferential orientation (if any) will continue as additional cells cycled to further capacity loss are characterized.

Conclusions

Work performed during this quarter largely involved setting up a process to resolve grain size and orientation in various cathode materials using EBSD. As the team moves forward with recovery and treatment of cathodes using different processes (chemical de-lithiation, electrochemical re-lithiation, etc.), we will evaluate relationship between performance and grain size/orientation.

Milestones and Deliverables

- Report summarizing methodology to build grain orientation maps for uncycled versus cycled cathode material (March 2019). *Status*: Complete
- Build EBSD map of chemically delithiated lithium nickel manganese cobalt oxide (NMC) from Argonne. (Sept. 2019)

Microcalorimetry on Recycled Materials

Matthew Keyser, Josh Major, Jeff Tomerlin, Shriram Santhanagopalan (NREL)

Background

The chemistries of advanced energy-storage devices are very sensitive to operating temperature. High temperatures degrade batteries faster while low temperatures decrease their power and capacity. NREL's equipment is sensitive enough to determine how changing the design of cell components affects the overall performance of the cell. We will use our isothermal calorimeters to develop an understanding of the life cycle effects on heat generation and determine if the recycling processes being developed under the ReCell program have a deleterious effect on the performance of the cells. In particular, NREL will be investigating the following:

- 4) Thermally characterize existing NMC cathode compositions to understand how the thermal signature of a battery changes from the beginning of life to the end of life. The data will be used to assess the quality of the recycled material being produced under the ReCell program.
- 5) Thermally characterize NMC/graphite cells with a known contaminant. For instance, we want to understand how much silicon material can be tolerated in the cathode without having a negative effect on heat generation and efficiency.
- 6) Match the extent and type of thermal degradation to target recycling methods, based on load profiles, cycling windows, and cost metrics.

Results

Initially, the amount of material being produced under the recycling processes will be limited. Thus, NREL needed to fabricate a microcalorimeter that was accurate enough to measure the heat signatures from pouch cells that are less than 50 mAh. The microcalorimeter developed for this and other DOE programs is shown in Figure 3. The microcalorimeter's design is based on NREL's R&D100 large cell format calorimeter design. The calorimeter shown is submerged in an isothermal bath that is controlled to within $\pm 0.001^\circ\text{C}$. The bath temperature can then be varied from -30°C to 60°C to assess the efficiency changes of the cell over the batteries operating range. The calorimeter was designed to allow a known pressure – up to 10 psi – to be applied to the cell under test to ensure consistent results.



Figure 3. NREL's microcalorimeter. Figure Credits, Josh Major, NREL

To assess the accuracy and resolution of the microcalorimeter, NREL cycled a single layer CAMP NMC523/graphite pouch cell with a capacity of approximately 30 mAh under a C/2 discharge. The results are shown in Figure 4. The microcalorimeter is showing noise levels of 200 μWatts but it is accurate enough to

clearly show the entropic heat signature of the cell when cycled at this rate. The heat generation, of course, will be dependent on the c-rate, current collector, cathode/anode particles, conductive fiber, and binder.

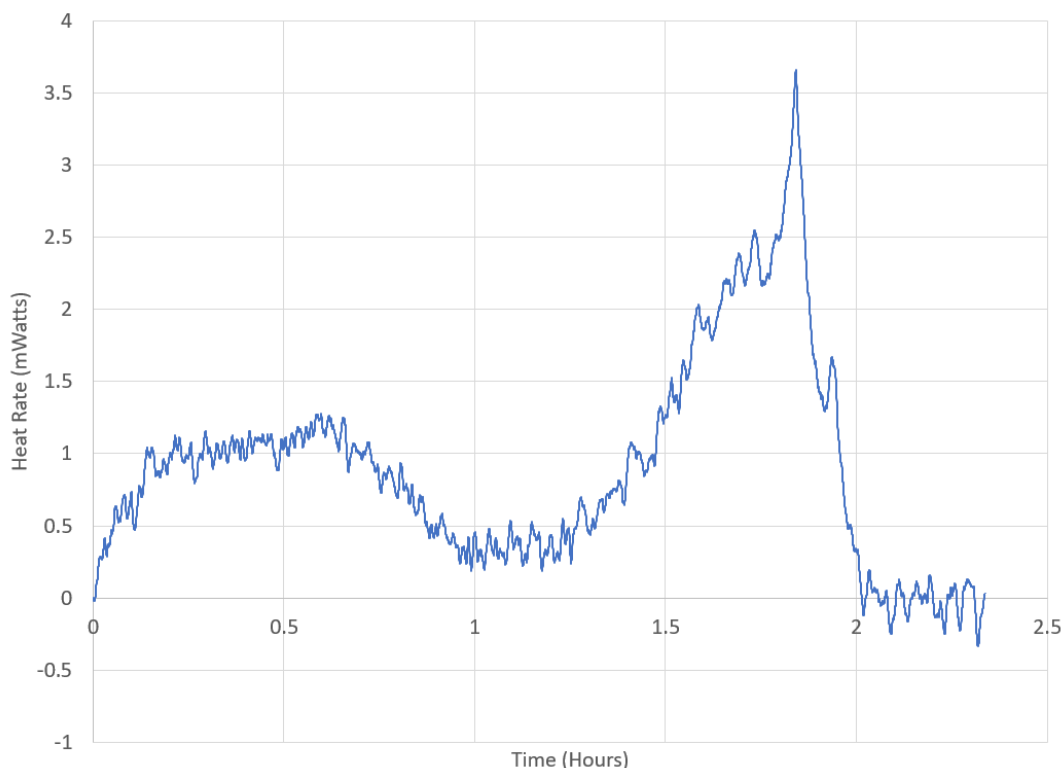


Figure 4. Heat generation of an NMC523/graphite cell under a C/2 constant current discharge. Figure Credits: Matt Keyser, NREL

Conclusions

Work performed during this quarter largely involved setting up the microcalorimeter. The noise level of the microcalorimeter is around 200 μ Watts and under controlled heater tests has an error of less than 2%.

In the next fiscal quarter, NREL will receive cells with pristine cathode/anode material. NREL will measure the heat generation at the beginning and end of life. The data from these tests will be used as a baseline to assess the performance of future recycled material and processes. NREL will also receive cells from Argonne with a known amount of contaminant on the cathode and anode. NREL will use calorimetry to determine how these contaminants affect the performance of the cells.

Milestones and Deliverables

- Thermal assessment of single layer pouch cells at the beginning and end of life. (June 2019)

Cost and Environmental Impact Modeling: EverBatt

Qiang Dai (Argonne)

Background

Cost and eco-friendliness are two crucial performance metrics for battery recycling technologies. Argonne has developed the EverBatt model to estimate the economic and environmental impacts associated with closed-loop recycling of lithium-ion batteries. We will use the model to evaluate the recycling processes and design-for-recycling (DfR) strategies developed under the ReCell Center, and thereby helping inform and direct the R&D efforts. Specifically, we will

- 1) Expand EverBatt to include unit processes proposed for direct cathode recycling and recovery of anodes and electrolyte components; and
- 2) Increase the granularity of the battery manufacturing module and the recycling module in EverBatt to enable evaluation of DfR strategies

Results

Since information on the recycling processes and DfR strategies that will be investigated under the Center is not yet available, during the first and second quarters of FY2019, we focused on improving the accuracy and usability of EverBatt. In particular, we have made several major updates to the EverBatt model, including (1) the background data based on the most recent version of BatPaC (version 3.1 June 28 2018) and GREET (version 2018), (2) energy and materials flows associated with pyrometallurgical (pyro) recycling, hydrometallurgical (hydro) recycling, and cathode powder production processes, based on new industry information, and (3) equipment cost data based on literature and publicly available database. We have also refined the cost calculation method, to account for safety factors in process design and product price margins.

Figure 5 shows the cost and environmental impact associated with the production of 1 kg $\text{LiNi}_{1/3}\text{Mn}_{1/3}\text{CO}_{1/3}\text{O}_2$ (NMC111) powder from materials recovered from pyro and hydro recycling processes, and those for 1 kg regenerated NMC111 powder through direct recycling process, normalized to those for 1 kg virgin NMC111 powder. The results indicate that if the spent batteries are transported as Class 9 hazardous waste over distances around 500 miles by trucks, and the throughput of the recycling plant is around 10,000 metric tons per year, which are both reasonable assumptions for current industry practices, conventional recycling technologies such as pyro and hydro are not likely to be economically feasible, nor would they offer considerable environmental benefits, except for SO_x emissions. In contrast, direct cathode recycling may represent the best opportunity to reduce the cost and environmental burdens of the cathode materials, as it is able to bypass the capital- and energy-intensive cathode powder production process, while this process is required for materials recovered from pyro and hydro recycling to close the loop.

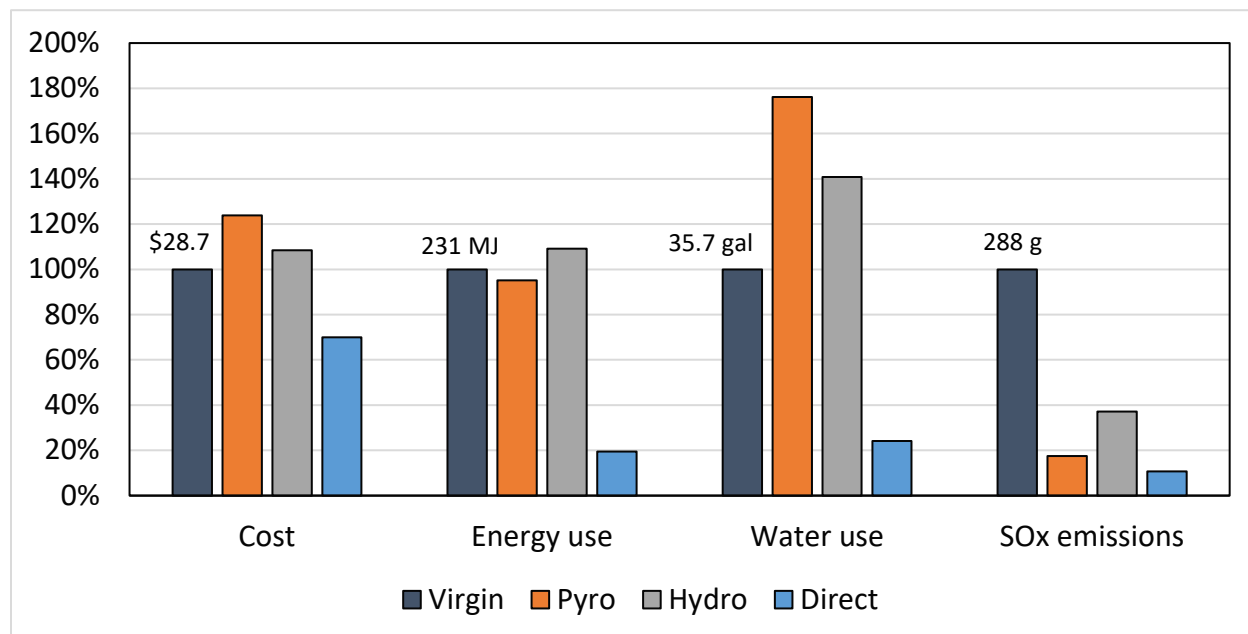


Figure 5. Cost and Environmental Impacts Comparison for 1 kg produced NMC111 powder

Conclusions

With updates on cathode powder production and pyro and hydro recycling processes in EverBatt, we found that conventional (pyro and hydro) closed-loop recycling routes are not as competitive with virgin production as we had previously thought. Industry information is key to improving the model accuracy. Although direct recycling seems to be a promising option, due to lack of industry data, its evaluation results in the current version of EverBatt are associated with large uncertainties. In the next quarter, we will focus on obtaining information on direct recycling and improving its modeling in EverBatt.

Milestones and Deliverables

- EverBatt report that documents methodology, assumptions, and data sources. *Status: Under Review*
- New version(s) of EverBatt that can evaluate recycling processes and DfR strategies developed under the ReCell Center. (May-Sept. 2019)

Supply Chain Analysis for Battery Recycling

Margaret Mann, Daniel Inman, Darlene Steward (NREL)

Background

Increasing demand for battery component materials combined with limited supply may put upward pressure on prices and limit the commercial potential for electrifying transportation. While industrial recycling of lithium ion batteries is economically viable and undertaken in many countries, the long-term implications of recycling on primary battery manufacturing and material supply are largely unknown. As R&D efforts to better recycle lithium ion batteries are undertaken, a birds-eye view of the interconnections between raw material availability, primary manufacture, recycling, and demand is needed.

In this project, NREL is incorporating previous analysis and data in a system dynamics framework, named LIBRA (Lithium Ion Battery Recycling Analysis), to explore issues related to the global and regional impacts of the interlinking supply chains associated with battery manufacturing and recycling. Electrification of the transportation and energy storage markets is projected to result in explosive growth in the demand for batteries. In response to concern over raw material demands, increased emphasis is being placed on battery recycling capacity expansion. While some resulting impacts are anticipated, such as the shift in manufacturing costs and raw material prices, the inter-connectiveness of multiple markets, operations, and policies could have unanticipated impacts on the success of electrification efforts. LIBRA analytically explores the technological and market feedback and feed-forward signals that could affect global supply chains for raw materials, primary and recycled batteries, and electric vehicles.

Results

Work performed this quarter has focused on the supply and demand relationships for cobalt and lithium, to evaluate the impact that recycling can have on material availability for electric vehicle manufacturing in the U.S. A draft user interface for the LIBRA model has been published at <https://exchange.iseesystems.com/public/danielinman/libra-01-demo/index.html#page1>. The user can vary the share of batteries manufactured with different battery chemistries to see how much of the U.S. demand for cobalt can be met with recycling, as well as how the estimated global reserves of cobalt are likely to change over time. U.S. and global sales of battery electric vehicles (BEV), plug-in hybrid electric vehicles (PHEV) are calculated as inputs based on multiple literature estimates and can be varied.

Current work in this project includes incorporation of the relationship between price signals from other industries on the supply of cobalt, as well as the impact of battery chemistry evolution on the economics of recycling. Figure 6 provides a schematic representation of the system dynamics (SD) model being developed.

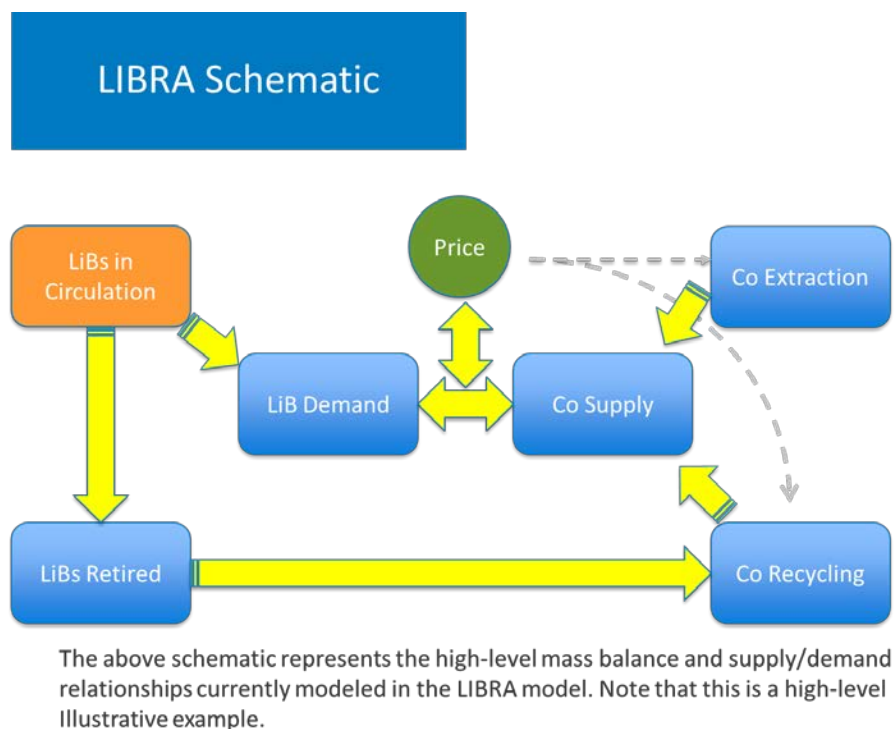


Figure 6: Schematic of the Lithium Ion Battery Recycling Analysis (LIBRA) Model. Mass balance and economic supply and demand relationships are used to calculate the values of materials and price in each box, as the quantity of lithium-ion batteries in circulation (orange box) is varied by the user.

Presentations and Publications:

Also as part of this quarter's work, NREL presented a summary of supply chain and economic competitiveness analysis at a Roundtable on Battery Recycling at Argonne, which was held as part of the ReCell Center ribbon cutting.

A paper called the Economics and Challenges of Li-Ion Battery Recycling from End-of-Life Vehicles will be published in *Procedia Manufacturing* following the 6th Global Conference on Sustainable Manufacturing held in Lexington Kentucky in October, 2018. Once published, a link will be provided to DOE.

A paper called The case for recycling: Overview and challenges in the material supply chain for automotive lithium-ion batteries will be published in a special issue of *Sustainable Materials and Technologies*, organized by Linda Gaines of Argonne National Laboratory.

Milestones and Deliverables

- Model Supply/Demand Relationship and create user interface for LIBRA (Q2)
- Evaluate investment decisions for recycling = $f(\text{price of Co, policies, cost of recycling technology, purity requirements, etc.})$ (Q3)
- Summarize material supply risk in a draft paper to DOE (Q4)

Cross-Cutting Activities – CAMP Facility Support

Erik Dahl, Alison R. Dunlop, Andrew N. Jansen (PI), Dave Kim, Bryant J. Polzin, Krzysztof Pupek, Stephen E. Trask (Argonne)

Background

Numerous recycled battery materials will be created in the ReCell Program that will need to be validated in prototype electrodes and pouch cells. The Cell Analysis, Modeling, and Prototyping (CAMP) Facility at Argonne will validate these materials (active cathode powders, graphite, electrolytes, etc.) and compare their electrochemical performance to baseline electrodes (and electrolyte). Validating the electrochemical performance of recycled battery materials will be critical to establishing their market viability.

In FY 2019, the CAMP Facility will use pristine NMC111 cathode material and SLC1520P graphite to fabricate baseline capacity-matched electrodes and baseline single-layer pouch cells. In addition, they will use chemically delithiated NMC111 pristine materials that are supplied by Argonne's Materials Engineering Research Facility (MERF) as tasked in the ReCell Program. The final delithiated NMC111 powder will also be fabricated into a baseline delithiated cathode electrode that is capacity matched to the baseline SLC1520P anode electrode. All of the electrodes will first be tested in coin cells for initial validation and then tested in single-layer pouch cells for rate performance, HPPC impedance, and cycle life. All future recycled NMC111 cathode materials will be compared against this baseline electrochemical performance data, as well as other recycled battery materials that are of interest to the ReCell Program.

Preliminary experiments will be conducted to test the effects of rinsing harvested electrodes from end-of-life pouch cells and reassembled into cells. These results will be of particular use to the Cell Design efforts focused on rejuvenating electrodes/cells via an "electrolyte flush".

Results

A large supply (60 kg) of NMC111 was purchased from Toda and distributed as requested to other efforts in the ReCell Program. The CAMP Facility fabricated sample electrodes of the baseline NMC111 powder to establish initial specific capacity values, which were needed in designing the final electrode couple. Meanwhile, MERF conducted scale-up experiments to chemically delithiate this baseline NMC111 powder. Samples of the delithiated powder were provided to CAMP Facility to make sample electrodes and coin cells for electrochemical performance analysis. These results are summarized in Table 1. This effort clearly demonstrated that the NMC111 powder was effectively delithiated and, more importantly, that this cathode powder is capable of being relithiated to its initial pristine capacity within three cycles.

Table 1. Formation Cycling results for Pristine (Baseline) and Delithiated NMC111 cathode powder.

NMC111 Half Cell	1 st Cycle Charge	1 st Cycle Discharge	1 st Cycle Efficiency	Reversible (3 rd) Cycle Charge	Reversible (3 rd) Cycle Discharge	Irreversible Capacity Loss
Average (3-4 cells each)	(mAh/g*)	(mAh/g*)		(mAh/g*)	(mAh/g*)	(mAh/g*)
Large Batch II Delith.	145	162	112 %	163	163	-17 (-12%)
Large Batch I Delith.	148	162	110 %	163	162	-14 (-9.7%)
Small Batch Delith.	153	160	104 %	161	160	-7 (-5%)
Baseline	184	162	88 %	163	162	21 (12%)

Capacity-matched single-sided baseline electrodes were designed and fabricated using the electrochemical results summarized in Table 1. Approximately 68.5 meters of cathode electrode was made using pristine NMC111 with a capacity loading of ~1.62 mAh/cm². Approximately 90 m of anode electrode was made using SLC1520P graphite with a loading of ~1.93 mAh/cm², followed by ~16 m of delithiated NMC111 (MERF, scaled-up) with a loading of ~1.63 mAh/cm². The details of these electrodes are summarized in Figure 1.

Cathode: A-C02190 wt% **Toda NMC111**

5 wt% Timcal C-45

5 wt% Solvay 5130 PVDF Binder

Toda NMC111, Electrode Library

SS = single sided [LN3174-71-4]

Al Foil Thickness: 20 µm

Total Electrode Thickness: 61 µm (SS)

SS Coating Thickness: 41 µm (SS)

Porosity: 33.5 %

Total SS Coating Loading: **11.22 mg/cm²**Total SS Coating Density: 2.74 g/cm³Estimated SS Areal Capacity: **1.62 mAh/cm²**[Based on rev. C/10 of 161 mAh/g for 3.0 to 4.3 V vs. Li]
Expected 1st de-lithiation capacity is **164 mAh/g** vs. Li metal**Cathode: LN3174-72-2**90 wt% **De-lithiated Toda NMC111**

5 wt% Timcal C-45

5 wt% Solvay 5130 PVDF Binder

De-lithiated Toda NMC111 provided by MERF

SS = single sided

Al Foil Thickness: 20 µm

Total Electrode Thickness: 61 µm (SS)

SS Coating Thickness: 41 µm (SS)

Porosity: 33.2 %

Total SS Coating Loading: **11.27 mg/cm²**Total SS Coating Density: 2.75 g/cm³Estimated SS Areal Capacity: **1.63 mAh/cm²**[Based on rev. C/10 of 161 mAh/g for 3.0 to 4.3 V vs. Li]
Expected 1st de-lithiation capacity is **145 mAh/g** vs. Li metal**Anode: A-A005B**91.83 wt% **Superior Graphite SLC1520P**

2 wt% Timcal C45 carbon

6 wt% Kureha 9300 PVDF Binder

0.17 wt% Oxalic Acid

Electrode Library, Prod: SLC1520P

SS = single sided [LN3174-74-4]

Cu Foil Thickness: 10 µm

Total Electrode Thickness: 55 µm (SS)

SS Coating Thickness: 45 µm

Porosity: 34.8 %

Total SS Coating Loading: **6.38 mg/cm²**Total SS Coating Density: 1.42 g/cm³Estimated SS Areal Capacity: **1.93 mAh/cm²**[Based on rev. C/10 of 330 mAh/g for 0.005 to 1.5 V vs. Li]
Expected 1st lithiation capacity is **300 mAh/g** vs. Li metal

Figure 1. Baseline single-sided electrodes fabricated by the CAMP Facility.

A coin-cell test matrix and test protocols were created to test the long-term electrochemical performance of the baseline electrodes (Figure 2). The baseline pristine NMC111 cathode is now under test in half-cells, followed by the baseline graphite and delithiated NMC111 electrodes. These results will be presented in the next quarter.

Run Order	Anode	Cathode	Electrolyte : Amount	Testing Protocol Order			
				Profile 1	Profile 2	Profile 3	Profile 4
1	Li	NMC111	Gen 2 : Flooded	ReCell-Cathode-Half-Form.000	ReCell-Cathode-Half-Rate.000	-	-
2	Li	NMC111	Gen 2 : Flooded	ReCell-Cathode-Half-Form.000	ReCell-Cathode-Half-Cyc.000	-	-
3	Li	Delithiated NMC111	Gen 2 : Flooded	ReCell-Cathode-Half-Form.000	ReCell-Cathode-Half-Rate.000	-	-
4	Li	Delithiated NMC111	Gen 2 : Flooded	ReCell-Cathode-Half-Form.000	ReCell-Cathode-Half-Cyc.000		
5	1520P	Li	Gen 2 : Flooded	ReCell-Gr-Half-Form.000	ReCell-Gr-Half-Rate.000	-	-
6	1520P	Li	Gen 2 : Flooded	ReCell-Gr-Half-Form.000	ReCell-Gr-Half-Cyc.000	-	-
7	1520P	NMC111	Gen 2 : 25 μ L	ReCell-FullCell-Form.000	ReCell-FullCell-Rate.000	ReCell-FullCell-HPPC.000	ReCell-FullCell-Cyc.000
8	1520P	NMC111	Gen 2 : 25 μ L	ReCell-FullCell-Age.000	-	-	-
9	1520P	Delithiated NMC111	Gen 2 : 25 μ L	ReCell-FullCell-Form.000	ReCell-FullCell-Rate.000	ReCell-FullCell-HPPC.000	ReCell-FullCell-Cyc.000
10	1520P	Delithiated NMC111	Gen 2 : 25 μ L	ReCell-FullCell-Age.000	-	-	-

Figure 2. Test matrix developed for evaluating ReCell baseline electrodes (see Figure 1) in coin-cell format.

Conclusions

The CAMP Facility is actively supporting the efforts of the ReCell Program by providing baseline materials and fabricating trial electrodes and baseline electrodes. It has established a thorough test matrix and protocols and has begun electrochemical evaluation of the three baseline active materials of interest to the ReCell Program in FY 2019. Future efforts will continue to test the baseline electrodes and recycled materials in coin cells and pouch cells as needed.

Milestones and Deliverables

Task 1 (M1-3): Fabricate >10 meters of single-sided paired electrodes (NMC111 & SLC1520P) with ~ 2 mAh/cm² to serve as baseline.

Task 2 (M4-9): Fabricate ~ 6 single-sided electrodes with recycled materials from team members as they become available.

Task 3 (M3-12): Assemble and test a total of ~36 single-layer pouch cells using electrodes from Tasks 1 & 2.

Task 4 (M4-12): Assemble and test a total of ~12 single-layer pouch cells using harvested and rinsed electrodes (for Cell Design).

References

None.

Cross-Cutting Activities – Post Test Facility Support

Nancy Dietz Rago, Zhenzhen Yang, Ira Bloom (Argonne)

Background

The Post Test Facility at Argonne performs a supporting role in the ReCell Program. Post-test diagnostics of aged batteries can provide additional information regarding the cause of performance degradation, which previously, could be only inferred. The facility combines microscopy, spectroscopy and chromatography in a controlled-atmosphere glove box to the greatest extent possible to characterize materials without air exposure. These results will help us identify issues in the recycled materials, such as how well does a given recycling process separate an initial mixture of cathode, anode, supporting foils and casing materials?

Results

Because we perform a supporting role, we depend on others for materials. This quarter we characterized pristine and chemically-delithiated $\text{Li}(\text{Ni}_{1/3}\text{Mn}_{1/3}\text{Co}_{1/3})\text{O}_2$ (NMC111) powders using scanning-electron microscopy (SEM), X-ray photoelectron spectroscopy (XPS) and elemental analysis.

The NMC111 powders were delithiated by reaction with ammonium persulfate. The extent of delithiation was approximately 10-15%. One of the first questions to be answered was, did the delithiation process change the properties of the material?

Figure 1 shows SEM micrographs of pristine and chemically-delithiated NMC111 particles. Comparing the size and morphology of the particles shows no obvious differences between the two types of particles.

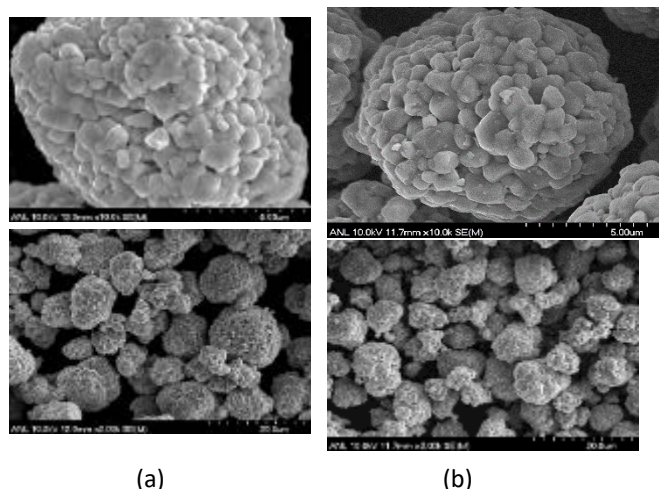


Figure 1. SEM micrographs of (a) pristine and (b) chemically-delithiated NMC111 particles.

Size analysis showed that the average particle size did not change during the delithiation process, as expected based on the SEM results, as shown in Figure 2. BET surface area measurements showed that the delithiation process did have an effect on the particles. The surface area of the pristine material was $0.37 \text{ m}^2/\text{g}$. After delithiation, the surface area increased to $0.83 \text{ m}^2/\text{g}$, most likely due to microcracks.

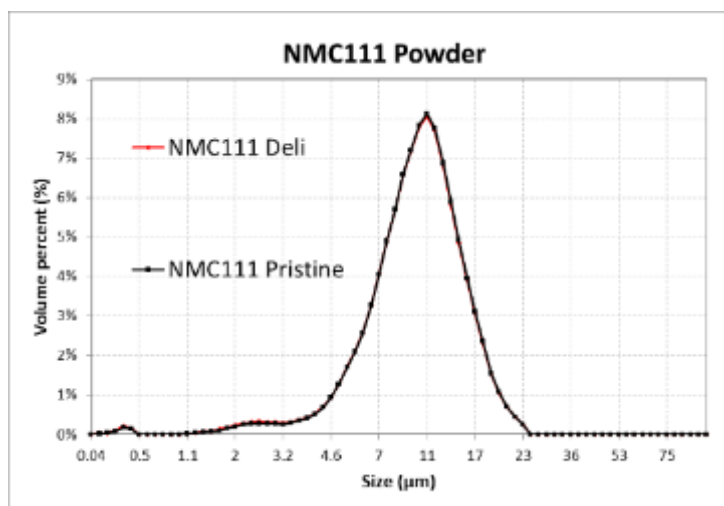


Figure 2. Results from particle size analysis.

The XPS results are shown in Figure 3. Comparison of the pristine and delithiated materials shows no difference in the Ni2p, Mn2p and Co2p transitions. A change in the XPS of oxygen was seen. Instead of two distinct oxygen peaks, at ~531 and ~528 eV, one of the peaks in the delithiated powder appears to have shifted to lower binding energy and merging with the other peak. This may indicate a change in the environment around oxygen. As far as the lithium environments are concerned, there appears to be some movement of the Li1s peak to lower binding energy, but the signal is too weak to be certain.

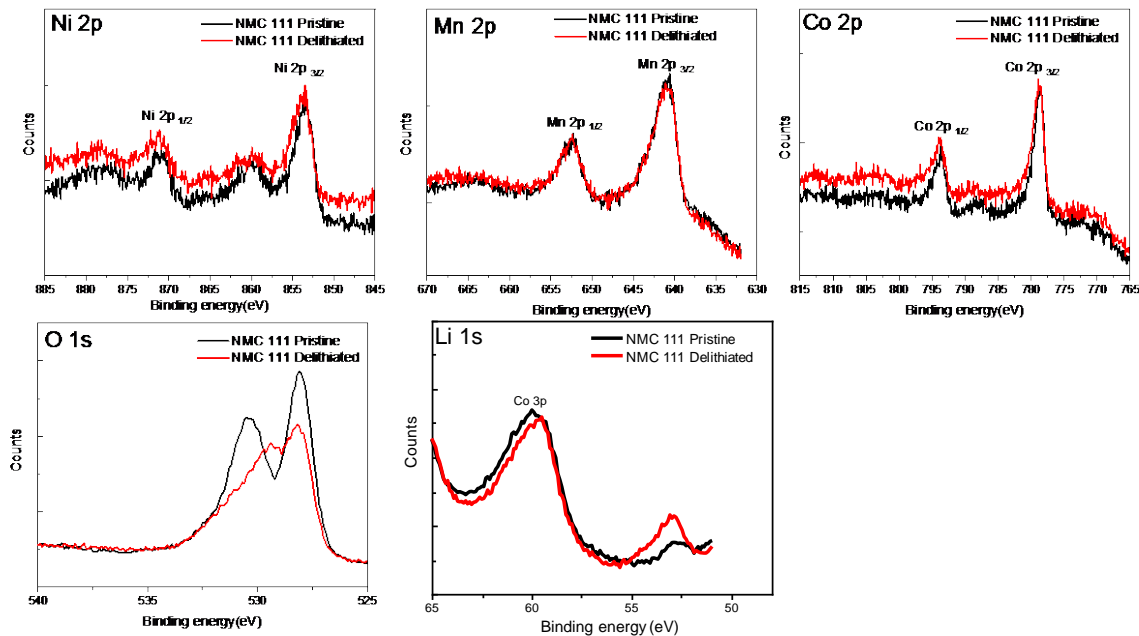


Figure 3. XPS results from pristine and chemically-delithiated NMC111. A change in the oxygen chemical environments was seen.

The X-ray diffraction (XRD) patterns from the pristine and the delithiated samples are shown in Figure 4. The lattice constants from the refinement of the diffraction data are given in Table 1. After chemical delithiation, the (003) peak shifted to a higher d-spacing value due to lattice expansion along the *c*-axis. There was a

decrease in the length of the a -axis of the hexagonal unit cell. This indicates that lithium ion extraction from the host structure created octahedral vacancies in the lithium layer. However, the overall volume change upon delithiation was only about 1%. The results indicate that the bulk crystal structure remained quite stable.

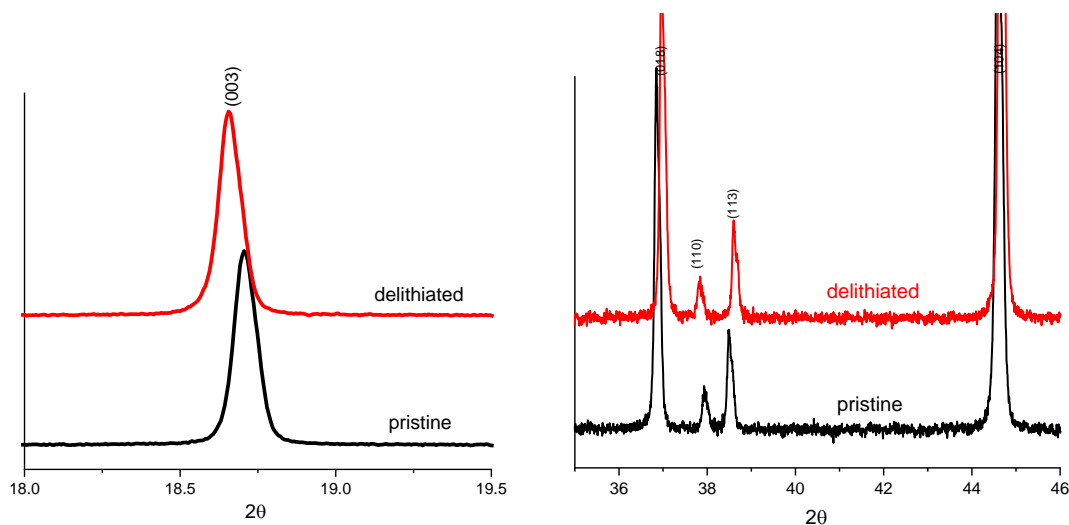


Figure 4. XRD pattern from the pristine and delithiated powders. There was an increase in the length the c -axis and a decrease in the length of the a -axis of the unit cell after delithiation.

Table-1: Lattice parameters, a and c , and volume from XRD refinement of pristine and chemically-delithiated NMC111 powders.

	a (Å)	c (Å)	Vol
Pristine	2.8585	14.226	100.67
Chemically-delithiated	2.8494	14.265	100.30

Because these powders form the basis of further experimentation, samples were chemically analyzed using inductively-coupled-plasma mass spectrometry (ICP-MS) to confirm the results obtained by others in the project. The results from the chemical analyses are given in Table 2.

Table-2: Results from ICP-MS analyses of pristine and chemically-delithiated NMC111 powders. The uncertainty in the values is $\pm 5\%$ of the reported value.

	Weight %			
	Li	Co	Mn	Ni
Pristine	7.36	19.8	17.9	19.8
Chemically-delithiated	6.63	20.3	18.4	20.2

Using these values and assuming that the mole fractions of cobalt, manganese and nickel sum to 1, the calculated formulae for the two materials are $\text{Li}_{1.099}(\text{Ni}_{1/3}\text{Mn}_{1/3}\text{Co}_{1/3})\text{O}_2$ and $\text{Li}_{0.972}(\text{Ni}_{1/3}\text{Mn}_{1/3}\text{Co}_{1/3})\text{O}_2$, respectively, for the pristine and delithiated powders. The extent of delithiation was 11.6%.

During the current quarter, we also characterized the effect of binder burn-out on the properties of NMC111. This sample was prepared by heating at $4^\circ\text{C}/\text{min}$ to 500°C ; holding at 500°C for 6 h; and cooling at $4^\circ\text{C}/\text{min}$ to

ambient. Air was flowing at 200 L/h through the furnace. SEM micrographs, shown Figure 5, revealed that the surface of the particles was covered by thin platelets, which by EDS, were rich in fluorine.

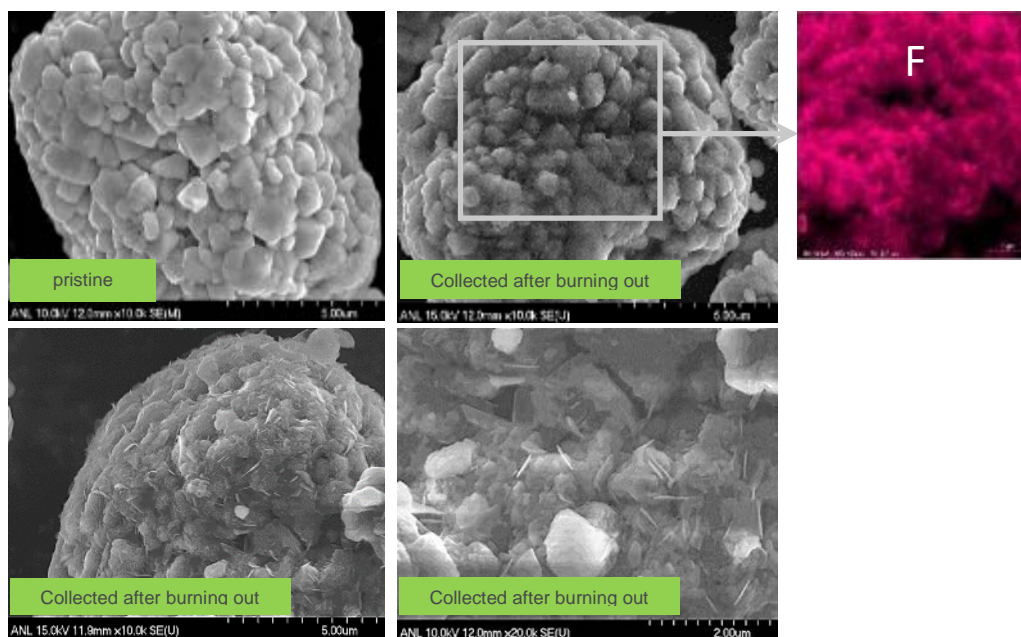


Figure 5. SEM micrographs of NMC111 powder before and after binder burn-out. A fluorine map (to the right) of the highlighted area in blue shows that the surface is rich in fluorine.

The powder was also characterized by XPS to determine changes in the surface chemistry. The results are shown in Figure 6 and are consistent with the presence of LiF and Li_2CO_3 on the surface of the NMC111 particles as a result of burning PVDF.

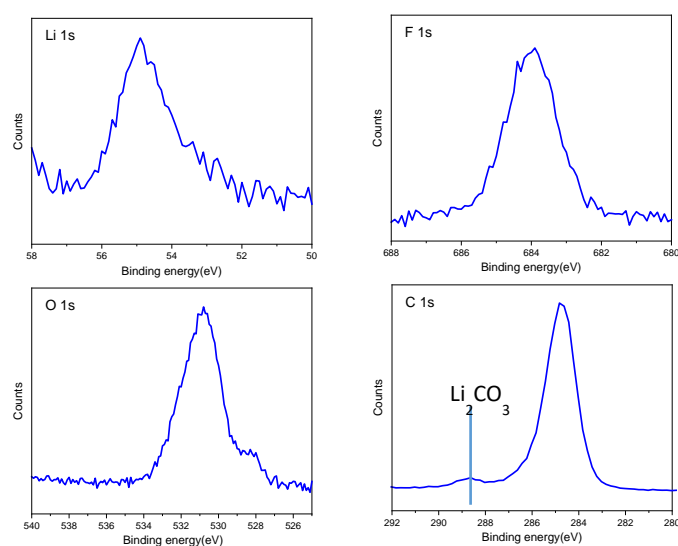


Figure 6. XPS results from the NMC111 powder after binder burn-out.

Comparing XRD patterns of the pristine material and the material after burn-out showed a change in the length of the a -axis by about 0.003 Å. From a refinement of the XRD data, the crystallographic parameters, assuming a hexagonal unit cell, were $a=2.8617$ Å and $c=14.226$ Å. The volume of the unit cell was 100.92 Å³. These were not significant changes.

The surface area of the powder after the burn-out process decreased. It was 0.29 m²/g, which was 0.08 m²/g less than that of the pristine material.

Cell disassembly will be an important part of the project. A how-to guide for taking pouch and 18650-sized cells apart was written and placed in the project's folder on Box. The guide should form the basis for a safe, common practice.

Conclusions

Characterization of pristine and chemically-delithiated NMC111 powders was performed using a number of techniques. No obvious changes were seen in particle size and morphology that were the result of the delithiation process. However, changes were seen in the oxygen environments by XPS. The surface area more than doubled as a result of the delithiation process. Changes in the crystallographic parameters were seen, indicative of vacancy formation. The extent of delithiation was determined to be 11.6% by wet-chemical analysis.

As a result of binder burn-out, the surface of the particles was covered with thin platelets that were rich in fluorine. XPS confirmed the presence of LiF and Li₂CO₃ on the surface of the particles.